Experimental Investigation of Surfactant-enhanced Washing and Supercritical CO_2 Extraction Processes for Waste Drilling Mud Remediation

by

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Abstract

Waste drilling mud is the second largest waste stream produced in the oil and gas industry after produced water and cannot be discharged or landfilled without proper treatment to meet regulatory requirements. Various contaminants are present in the waste drilling mud, including petroleum hydrocarbons, heavy metals, BTEX (benzene, toluene, ethyl benzene, and xylenes), polycyclic aromatic hydrocarbons (PAHs), and other hazardous materials typically originating from the base drilling fluids. Strict environmental regulations are in place regarding the disposal of the waste drilling mud and cuttings to minimize their effect to the environment. Therefore, the waste drilling mud must be properly treated before being released into the environment. Different technologies have been proposed for waste drilling mud remediation; however, most of them are unable to meet the strict environmental regulation limits.

In this thesis, different technologies to treat the waste drilling mud are reviewed. After a technical comparison, physical treatment technologies were selected as the most suitable methods. The main aim of this study is to investigate the abilities of the methods of surfactant-enhanced washing and supercritical CO_2 extraction, to treat the waste drilling mud and remove the hazardous petroleum hydrocarbons to meet the strict environmental regulations. The specific objectives of the study are to: (1) characterize the waste drilling mud using particle size distribution, X-ray diffraction (XRD), inductively coupled plasma optical emission spectrometer (ICP-OES), scanning electron microscope (SEM), and gas chromatography GC analyses; (2) identify of the most efficient, environmentally-friendly, and cost-effective technologies to treat the waste drilling mud; (3) screen and select the best

surfactants for drilling mud remediation using interfacial tension and sorption analyses; (4) experimentally determine the impacts of significant factors on the efficiency of the two physical processes, surfactant-enhanced washing and supercritical CO_2 extraction (SCE); (5) optimize both the surfactant-enhanced washing and supercritical CO_2 extraction processes; and (6) evaluate both the physical treatment processes considering efficiency, environmental impacts, and possible separation and/or recovery of hydrocarbons.

A technical review was completed by considering key factors in an efficient process for waste drilling mud remediation, including efficiency, particle size effect, environmental impact, cost, energy requirement, and processing time. Surfactant-enhanced washing and supercritical CO_2 extraction were selected as two viable, efficient, and environmentally-friendly physical treatment methods. Three surfactants, one anionic (Alfoterra 145-8S 90), one non-ionic (Triton 100), and one biosurfactant (Saponin), were experimentally analyzed, and Triton 100 (TX-100) was selected as the best surfactant based on the interfacial tension and sorption analyses. Experiments were conducted to investigate the effect of different parameters on the surfactant-enhanced washing process' efficiency, using Triton 100 as the most suitable surfactant, including (i) contact time, (ii) surfactant concentration, and (iii) temperature, and to obtain the optimized operating conditions. The supercritical CO_2 extraction experiments were also designed and conducted to investigate the effects of three parameters, including (i) temperature, (ii) pressure, and (iii) contact time on the process' efficiency.

The result of this study suggested that even though the surfactant-enhanced washing was able to remove up to 70% of the petroleum hydrocarbons, the process could not be

employed to treat the waste drilling mud to meet the landfilling regulations. The supercritical CO_2 extraction process, however, was capable of removing the petroleum hydrocarbons up to more than 97% when operated at the optimized conditions and could effectively remediate the waste drilling mud considering the initial total petroleum hydrocarbon concentration).

Based on the results of this study, supercritical CO_2 extraction (SCE) process was recommended as an efficient and environmentally-friendly method to remove the total petroleum hydrocarbons from the waste drilling mud to meet the provincial, national, and universal environmental regulations. The SCE process could easily separate the hydrocarbons from the waste mud effectively and in a short amount of time. The supercritical CO_2 extraction process could be tested and implemented for other contaminated substances with petroleum hydrocarbons as well. Although further investigation may be required, the results of this study can be a guide for future research on similar remediation processes.

Dedication

I dedicate my Ph.D. dissertation to my parents, Mohammad and Zahra, whose ongoing love and support have continuously motivated me to achieve higher levels of education.

I also dedicate this thesis to my lovely wife, Shirin, who has always believed in me. None of this would have happened without her help and constant encouragement.

I would also like to dedicate this dissertation to Sam, my newborn baby who has recently illuminated my life.

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List of Abbreviations

2FI	Two factor interaction
ACS	American chemical society
ANOVA	Analysis of variance
API	American Petroleum Institute
BBD	Box-Behnken design
BET	Brunauer–Emmett–Teller analysis
CCD	Central composite design
CCME	Canadian council of ministers of the environment
CEC	Cation exchange capacity
CI	Confidence interval
CMC	Critical micelle concentration
DCM	Dichloromethane
EDX	Energy dispersive X-ray spectroscopy
EOR	Enhanced oil recovery
EPA	Environmental protection agency
FID	Flame ionization detector

GC	Gas chromatography
HFC 134a	1,1,1,2-tetrafluoroethane
HOC	Hydrophobic organic compound
ICP-OES	Inductively coupled plasma optical emission spectrometer
IFT	Interfacial tension
LSDA	Lime soap dispersing agent
NADF	Non-aqueous drilling fluid
NRC	National research council
OSPAR	Oslo and Paris convention
PAH	Polycyclic aromatic hydrocarbon
PHC	Petroleum hydrocarbons
QAQC	Quality assurance and quality control
ROC	Retention on cuttings
RSM	Response surface methodology
SBF	Synthetic-based fluid
SCE	Supercritical CO_2 extraction
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope

SEW	Surfactant-enhanced washing
SFC	Supercritical fluid chromatography
SFE	Supercritical fluid extraction
TOC	Total organic carbon
USD	United States dollars
USEPA	United States environmental protection agency
WBF	Water-based fluid
XRD	X-ray diffraction

Chapter 1: Introduction

1.1 Background and motivation

Drilling mud is employed to balance subsurface pressures, lubricate the drill tool, and to carry drill cuttings to the surface. When the well is drilled, the used drilling fluid and the drill cuttings (solid rock pieces) are returned to the surface where they are separated using a shale shaker. Rocks and larger solid particles (drill cuttings) are separated from the mud containing fine particles and drilling fluids. Drilling waste, containing cuttings and drilling fluid, is the second largest waste volume produced by oil and gas operations behind produced water (Reis, 1993; Haut et al., 2007; Onwukwe and Nwakaudu, 2012), thus requires a great deal of attention due to its toxicity and its adverse impacts on the environment (Sil et al., 2010). Drilling mud contains variety of hazardous additives and is thus considered the main source of waste (Almudhhi, 2016; Ma et al., 2016). Depending on the type of drilling fluid used, the produced mud contains various levels of drilling fluid, reservoir fluids, and any production and treatment chemicals, either in the aqueous/oil phase or retained on the surface of the suspended solids. Other problematic substances include heavy metals with levels varying according to geological formation and chemicals used in productions. The multi-phase nature of the mud, water, dispersed and dissolved hydrocarbons/drilling fluid, and solids present challenges for offshore treatment and onshore disposal.

The purpose of drilling mud treatment processes is liquids/hydrocarbon removal, which typically decreases toxicity and volume. Thermal treatment (Carignan and Lake, 2007; Carignan et al., 2007; Fang et al., 2007; Pierce et al., 2006), biological degradation (Eia and Hernandez, 2006; Imevbore et al., 2000; Marks et al., 1988; Perie et al., 1995; Rojas-Avelizapa et al., 2007; Sliwka et al., 2012; Wysocki et. al., 2005), surfactant-enhanced washing (Carey, 2002; Childs et al., 2005; Hou et al., 2013; Muherei and Junin, 2007; Perry and Griffin, 2001; Xie et al., 2013; Xie et al., 2014; Yan et al., 2011), supercritical carbon extraction (Eldridge, 1996; Goodarznia and Esmaeilzadeh, 2006; Khanpour et al., 2014; Saintpere and Morillon-Jeanmaire, 2000; Seaton and Hall, 2005; Street and Guigard, 2006; Street et al., 2007), solidification and stabilization (Al-Ansary and Al-Tabbaa, 2007a; Al-Ansary and Al-Tabbaa, 2007b; Chen et al., 2014), membrane and forward osmosis treatments (Asatekin and Mayes, 2009; Codaya, 2014; Hickenbottom, 2013) are discussed in the literature review chapter as possible methods to remove hydrocarbons from the waste drilling mud. However, given the slurry nature of the drilling mud and high petroleum hydrocarbon concentrations, it is typically difficult to bring the contaminant levels to meet typical non-hazardous landfill limits. Therefore, the goal of this research is to identify and develop an optimized process to treat the drilling mud to meet landfill limits.

As the drilling mud is a slurry, the first step is to use a centrifugal separation to recover most of the fluid from the polluted solid particles. The second step is to separate entrained/trapped, adsorbed hydrocarbons from the solid particles. Among the methods suggested for the remediation of this waste, surfactant-enhanced washing has been reported to be an efficient method to remove hydrocarbons, organic compounds and heavy

metals from soil, sediments, and drilling mud and cuttings; however, as a standalone process, it is usually ineffective to meet the landfilling regulations. It was also reported to be an economically feasible method and is easy to implement. On the other hand, supercritical fluid extraction was also tested and some satisfactory results were reported for total petroleum hydrocarbon removal.

This study, therefore, focuses on investigating two physical treatment methods, surfactant-enhanced washing and supercritical CO_2 extraction processes, to remove the petroleum hydrocarbons from the waste drilling mud to meet the strict environmental regulations. This research is the result of a project proposed for the 2014-15 Leslie Harris Centre MMSB Waste Management Applied Research Fund with the collaboration of Universal Environmental Inc. in Newfoundland and Labrador. The waste drilling mud employed in this study came from the offshore production facilities in Newfoundland and Labrador. Since there is no treatment plant in the province to treat the drilling waste produced from the offshore industry, this research provides a great opportunity to investigate the possibility of providing a methodology to locally remove petroleum hydrocarbons from the waste drilling mud in a cost-effective and environmentally-friendly process.

1.2 Statement of problem

Several technologies have been proposed for the remediation of waste drilling cuttings and waste drilling mud; however, most of them are either unable to treat the waste drilling mud to meet the strict environmental regulations for landfilling or possess significant adverse

impacts on the environment. Therefore, there is a need to investigate the development and optimization of various treatment options on the waste drilling mud sample to identify a cost effective and environmentally-friendly method to effectively remove the petroleum hydrocarbons from the waste drilling mud. A complete understanding of various technologies is required to compare their behaviour and identify the most effective and environmentally-friendly process.

Surfactant-enhanced washing and supercritical CO_2 extraction are two technologies which can be employed to treat the waste drilling mud. The most suitable surfactant and the optimized operating conditions should be identified to optimize the surfactant-enhanced washing process. To date, there is little research conducted on the selection of the most suitable surfactant for such a process employing interfacial tension and sorption analyses. There has also been lack of sufficient research on the experimental investigation of both processes for the waste drilling mud and comparison of their capabilities to remove different fractions of petroleum hydrocarbons considering various significant effective parameters.

The current study focuses on: (a) conducting a technical comparison on different treatment technologies; (b) identifying the best surfactant for surfactant-enhanced washing of waste drilling mud by interfacial tension and sorption analyses; (c) the optimization of both surfactant-enhanced washing and supercritical fluid extraction processes considering three significant parameters for each process.

1.3 Objectives of the research

Drilling mud is a hazardous substance which cannot be landfilled in many jurisdictions due to the presence of toxic hydrocarbons and heavy metals. Environmental regulations regarding the disposal of drilling mud into land and marine environments are justifiably becoming stricter and a solution to treat this type of waste must be identified. Although there are a variety of methods proposed, most of them can barely meet the landfilling regulations in an effective environmentally-friendly manner. The goal of this research is to develop and optimize the treatment of waste drilling mud to meet the strict environmental regulations. The specific goals of this research are to conduct a technical assessment to identify the two most suitable methods by analyzing the treatment methods individually, and to experimentally optimize both processes and compare the experimental results of both processes to remediate the waste drilling mud to meet the landfilling regulations.

The tasks of this study are listed as follows:

- Characterize the waste drilling mud provided by Universal Environmental Inc. from offshore, Newfoundland and Labrador using ICP, SEM, Particle Size Distribution, XRD, and Gas Chromatography analyses;
- Conduct a technical comparison between different proposed technologies to treat the waste drilling mud such as thermal, chemical, physical and biological techniques, and select the most viable processes, considering effective factors, including efficiency, environmental impacts, cost, and processing time;

- Identify the most suitable surfactant for the waste drilling mud surfactant-enhanced washing among three proposed surfactants by interfacial tension and sorption analyses;
- Optimize the surfactant-enhanced washing process considering three effective parameters, namely contact times, surfactant concentrations, and temperature;
- Investigate the ability of the supercritical CO_2 extraction process to remove total petroleum hydrocarbons from the waste drilling mud;
- Optimize the supercritical CO_2 extraction process considering three key parameters: contact time, pressure, and temperature;
- Compare the experimental results of both surfactant-enhanced washing and supercritical CO_2 extraction processes to select the most suitable remediation process for the waste drilling mud.

1.4 Novelty and research contributions

Both surfactant-enhanced washing and supercritical extraction processes are well-known techniques for environmental remediation. Various studies have been conducted on both technologies for different types of wastes, especially for contaminated soil remediation. The aim of the current research was to investigate the applicability of both these processes for the remediation of an industrially-produced synthetic-based waste drilling mud and employ novel techniques to fill the research gaps.

Despite the various research reported on the use of different surfactants for the treatment of waste drilling mud, there is no or little research on the use of defined effective screening

criteria for selection of the most suitable surfactant. Furthermore, there is barely any discussion on the sorption analysis and its impact on the waste drilling mud remediation by surfactant-enhanced washing. These gaps have been addressed in the current dissertation.

Despite the research conducted on the application of supercritical fluid extraction on waste drilling mud treatment, there is no or little research present on the synthetic-based waste drilling mud and the effect of supercritical CO2 extraction on the removal and recovery of different fractions of the petroleum hydrocarbons. Research results on the waste remediation also significantly varies for different types of wastes and lack consistency. The effect of temperature, pressure, contact time and their possible co-interactions were also missing from the literature. These gaps were investigated in the current thesis.

1.5 Approach

An in-depth analysis of different waste drilling mud treatment processes, their limitations, and a thorough investigation on how to improve the processes were all conducted in the initial stages of this study. Characterization of the waste drilling mud was subsequently completed to achieve a thorough understanding of the composition, particle size distribution, BET surface, hazardous nature, moisture content, pH, electrical conductivity, and density of the sample.

The surfactant selection stage started with the interfacial tension and sorption analyses on three surfactants (Triton 100, Alfoterra 145-8S 90, and Saponin) to select the most suitable

surfactant for the surfactant-enhanced washing. The effect of temperature and adding another surfactant as an additive (sodium dodecyl sulphate) were also investigated in their capability of reducing the interfacial tension in oil/aqueous phase.

The effective parameters and their levels for the surfactant-enhanced washing process were identified based on a literature review on waste drilling mud, cuttings or contaminated soil surfactant-enhanced washing. Washing experiments were conducted to optimize the surfactant-enhanced washing process considering three significant parameters, including surfactant concentration, contact time, and temperature.

The results of the surfactant-enhanced washing process using Triton 100 were obtained by comparing the gas chromatography (GC) results (based on Tier 1 method (CCME, 2007) before and after the surfactant-enhanced washing. The effects of each parameter on the performance of the surfactant-enhanced washing process were also determined.

Supercritical CO_2 extraction experiments were also designed (using Box-Behnken design) and conducted, and the process was optimized considering temperature, pressure, and contact time as the significant parameters affecting the process' efficiency on petroleum hydrocarbon removal.

It should also be noted that research for the treatment of waste drilling cuttings and waste drilling mud is ongoing and further investigations on the technical, economical, and social implications are required to implement the results of this study.

1.6 Outline of the thesis

This thesis is divided into six chapters. Chapter 1, entitled “Introduction”, presents the background and motivation, objectives, and the approach to the development and optimization of the most suitable treatment process for waste drilling mud used in this study. The current state of the research on the waste drilling mud treatment is reported in Chapter 2, entitled “Literature Review”, where the basics of the drilling fluid, different types, its composition, generation of waste drilling mud and its history, treatment technologies, including their advantages, limitations and areas of improvements, adverse environmental impacts, and landfilling regulations are all reviewed. In Chapter 3, entitled “Characterization of the Waste Drilling Mud”, information is provided on characteristics of the waste drilling mud sample employed in this study, and the experimental and analytical procedures are described in detail, including how the waste drilling mud was characterized using numerous analyses. Chapter 4 presents how the best surfactant was selected based on interfacial tension and sorption analyses and how the surfactant-enhanced washing process was optimized considering contact time, surfactant concentration, and temperature as three significant parameters. Chapter 5 provides detailed information on how the supercritical CO_2 extraction process was developed and optimized considering contact time, pressure, and temperature as the most significant factors affecting the efficiency of the process. Comparison of the two optimized processes, the concluding remarks, and the final recommendations of the dissertation for further studies are all given in Chapter 6.

Chapter 2: Literature Review

2.1 Overview

In this chapter, waste drilling mud and its composition and production are described in detail and different technologies to treat the waste drilling mud are discussed. The advantages and limitations of these treatment processes are reviewed. Various environmental regulations around the world on drilling waste disposal and landfilling are listed. At the end of the chapter, a comparison of different technologies is conducted based on various factors, including efficiency, processing time, cost, safety issues and environmental impacts, and it is discussed why the physical treatment processes should be experimentally tested to investigate their ability to effectively remove the petroleum hydrocarbons (PHCs) from the waste drilling mud to meet the strict environmental regulations.

2.2 Drilling mud production

Drilling fluids are used to prevent the blowouts, balance and control formation pressure, minimize formation damage and corrosion, lubricate, cool, and remove the drill cuttings from the well by transporting them through the drill string, and up the annulus to the surface (Shaikh, 2010). The drilling mud is separated from the drill cuttings in a shale shaker. The drilling mud is a solid-liquid slurry with very high viscosity, high oil content, heavy metals, and other ingredients such as bentonite, barite, and other polymers (Khodja

et al., 2010; Wada et al., 2006). Figures 2.1 and 2.2 illustrate the drilling fluid injection and recovery system and the shale shaker respectively.

Figure 2.1 shows that the drilling fluid, stored in the mud pit, is pumped into the discharge line and goes down the drill-string to the drill-bit. At the drill-bit, the drilling fluid jets out of the openings or nozzles. The drilling fluid removes cuttings away from the drill-bit and then return via 'the flow-line'. The flow-line goes to the shale shaker where coarse particles are separated from the mud containing fine particles by a porous vibrating screen (Hossain and Al-Majed, 2015). Figure 2.2 illustrates the shale shaker, a vibrating screen which is typically the first solid/liquid separation device drilling waste encounter and removes most of the larger solids (Raja, 2012). When the drilling waste (mud and cuttings) enters the top of the shale shaker screen, most of drill cuttings are removed and drilling mud flows through the screen for re-use (ASME Shale Shaker Committee, 2011).

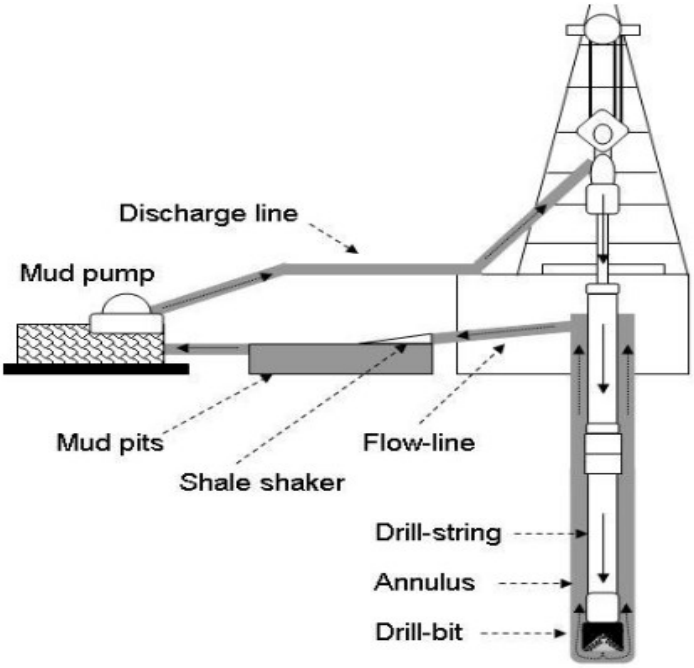


Fig. 2.1 – Drilling fluid injection and recovery system (Growcock and Harvey, 2005)

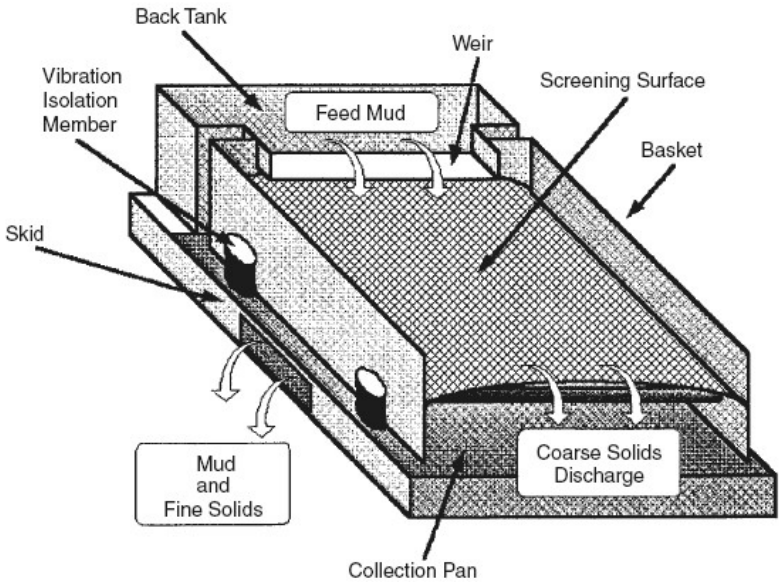


Fig. 2.2 - Shale shaker, separating coarse particles from fine solids (Nashaat, 2010)

2.3 Composition of the waste drilling mud

The composition of the waste drilling mud is complex (Ma et al., 2016) and dependent on the type of the drilling fluid in use. Although the composition of various types of waste drilling mud may significantly differ; their roles in drilling processes remain the same (Agwu and Akpabio, 2018). The geological formation of the drilled rock can also change the composition of the waste drilling mud. For instance, deeper wells increase the complexity of the produced drilling mud (Fink, 2011; Pettersen, 2007). The drilling fluid types are being discussed as they affect the metal concentration and contamination of the waste drilling mud. There are two primary types of drilling fluids: non-aqueous drilling fluids (NADFs) and water based fluids (WBFs) (Hossain and Al-Majed, 2015).

2.3.1 Non-aqueous drilling fluids

These types of drilling fluids are emulsions where the base fluid is synthetic oil, diesel fuel or mineral oil, with water and chemicals as the internal emulsified phase. A typical composition of non-aqueous drilling fluids is illustrated in Figure 2.3(a).

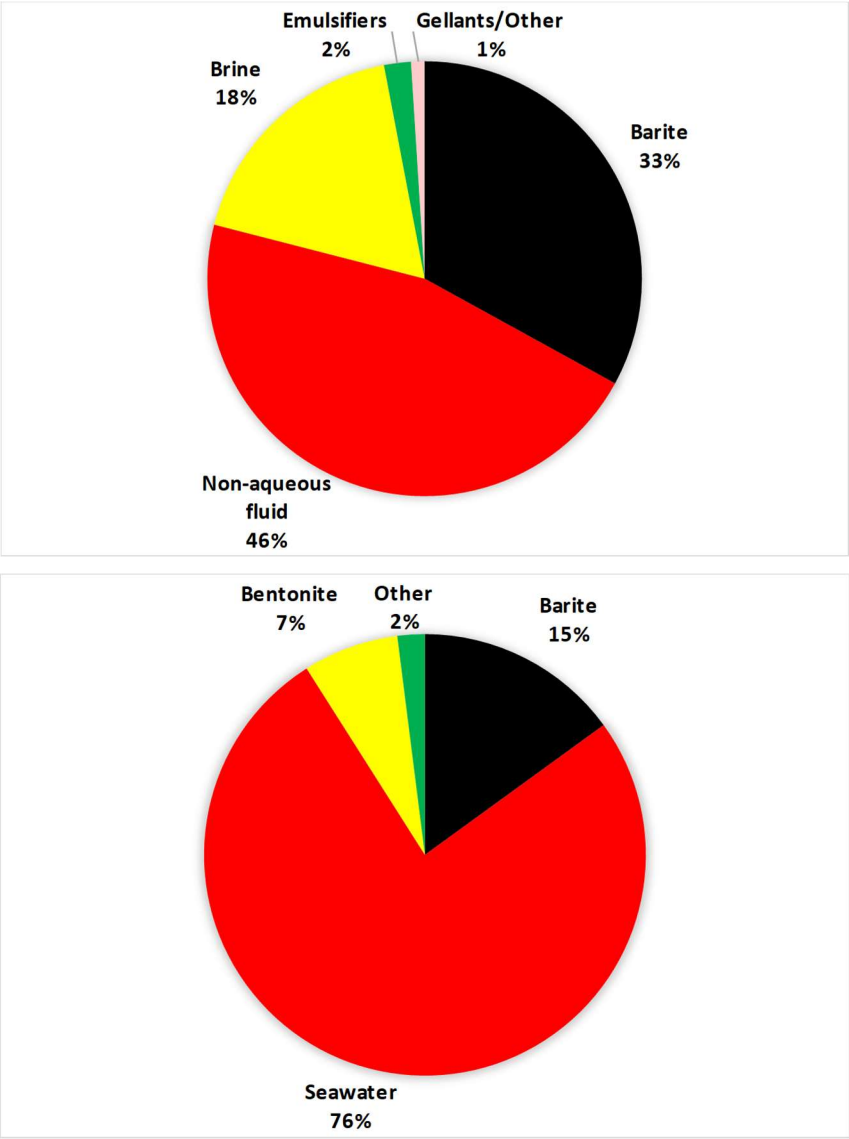


Fig. 2.3 – Typical composition of the (top) non-aqueous and (bottom) water-based drilling fluids (Force, 2009)

Several additives are added to control the properties of non-aqueous drilling fluids. Emulsifiers are employed for stabilizing the water in oil emulsions, barite is used to provide sufficient density, and clay materials are added to control the viscosity. There is

no need for lubricating materials in non-aqueous drilling fluids, as the base fluid provides sufficient lubricity. The physical characteristics of non-aqueous drilling fluids are outlined in Table 2.1. The brine in non-aqueous drilling fluids can contain various salts with different hazard classification, listed in Table 2.2.

Table 2.1 – Toxicity of typical compounds in non-aqueous drilling fluid (Force, 2009; Hossain et al., 2013)

Primary Function	**Type of material**	**Hazard classification**
Base fluids	Mineral oils, diesel, synthetic fluids (e.g. olefins, linear paraffin)	• Harmful • Possible eco-toxicity (fate dependent)
Weighting materials	Barite (typically), ilmenite, hematite, calcium carbonate	• Harmful • Hazardous nature causing environmental problems • Contain hazardous metals • Dust hazard
Primary emulsifier	Hydrophilic and hydrophobic compounds in a carrier fluid	• Harmful • Harmful to skin, eyes • Aspiration risk • Hydrocarbon-based carrier fluid
Secondary emulsifier	Hydrophilic compounds with a positive end in a carrier fluid	• Harmful • Irritating to skin and eyes • Aspiration risk • Hydrocarbon-based carrier fluid
Wetting agents	Hydrophilic compounds, sulphonic acid, amides, polyamides	• Harmful • Skin and eye irritation • May contain hydrocarbon-based carrier fluid
Viscosifiers	Organophillic montmorillonite, synthetic polymers	• Harmful • Dust hazard • Skin and eye irritation

Table 2.2 – Typical composition of sea water (Force, 2009)

Salt type	**Formula**	**Hazard classification**
Potassium chloride	KCl	Not classified
Sodium chloride	NaCl	Not classified
Sodium formate	NaCOOH	Eye irritant
Calcium chloride	$CaCl_2$	Not classified
Potassium formate	KCOOH	Not classified
Sodium bromide	NaBr	Not classified
Calcium bromide	$CaBr_2$	Not classified
Zinc bromide	$ZnBr_2$	Corrosive
Caesium formate	CsCOOH	Harmful/Irritant

Non-aqueous drilling fluids are classified based on their aromatic hydrocarbon concentrations. They can be further divided into oil-based fluids and synthetic based fluids. Oil based drilling fluids are defined by the presence of polycyclic aromatic hydrocarbon (PAH) levels, typically greater than 0.35%. The PAH content of diesel-based fluids is typically in the range of 2-4% and the aromatic content is up to 25%. When the conventional mineral oil is used as the base fluid, the total amount of aromatic hydrocarbons is half of a diesel-based fluid and the polycyclic aromatic hydrocarbon contents are 1-2% (Melton et al., 2000). Low toxicity mineral oil based fluids were developed after environmental concerns over the potential toxicity of diesel-based fluids. The polycyclic aromatic hydrocarbon content is less than 0.35% and greater than 0.001% (Melton et al., 2000). Synthetic based fluids (SBFs) contain negligible polycyclic aromatic hydrocarbons (less than 0.001%) and are produced by chemical reactions of relatively pure

components and can include synthetic hydrocarbons such as olefins, paraffin, and esters (Melton et al., 2000).

2.3.2 Water-based drilling fluid

Water-based drilling fluids consist of water mixed with bentonite clay and barium sulphate (barite) to control mud density. Other chemicals are added to gain the desired drilling properties, such as thinners, filtration control agents, and lubrication chemicals (HSE, 2000). The composition of water-based drilling fluids depends mainly on the density of the produced drilling fluid. United States National Research Council (NRC) estimated the composition of a typical water-based fluid with a density of 1,190 kg/m^3 to be 76 wt. % water, 15% barite, 7% bentonite, and 2% salts and other additives. Figure 2.3(b) illustrates a typical composition of water-based drilling fluids (Force, 2009).

The information on the toxicity of different additives in a typical water-based drilling fluid is listed in Table 2.3. Water is employed as the non-hazardous base fluid and most of the additives do not possess high toxicity to humans and the environment. Disposal of water-based drilling mud is usually allowed by the authorities due to the limited adverse impacts on the environment.

Table 2.3 – Toxicity of common additives to water-based drilling fluids (HSE, 2000; Force, 2009)

Additive compound(s)		**Toxicity information**
Water	Fresh water	not hazardous
	Sea water	low hazard potential
	Brine	see osmotic (salts)
	Saturated NaCl	low toxicity except in very high concentrations
Osmotic (salts)	$CaCl_2$	low acute toxicity
	KCl	low acute toxicity
	ZnBr/CaBr	severe skin or eye irritation
	Formates (NaCOOH, KCOOH)	low acute toxicity
Density	Barite (Barium sulphate)	low to moderate acute toxicity
	Calcium carbonate	low acute toxicity
	Iron carbonate	low to moderate acute toxicity
	Hematite	insufficient data available
	Ilmenite	no toxicity
Viscosity	Bentonite	low acute toxicity
	Organophilic clay	low acute toxicity
	Biopolymers	low toxicity
	Carboxymethyl cellulose	low toxicity
	polyanionic cellulose	low toxicity
	Guar gum (polysaccharide)	low toxicity
Dispersant	Modified polyacrylates	different toxicological properties
	Lignosulphonates	low toxicity
	Tannins	low acute toxicity

Fluid loss prevention	Synthetic polymers	different toxicological properties
	Carboxymethyl cellulose	low toxicity
	Polyanionicl cellulose	low toxicity
	Starch	low toxicity
	Bentonite	low acute toxicity
	Modified lignites	different toxicity depending on the modification
	Asphalt	low toxicity
	Resins	different toxicological properties
	Gilsonite	Concerns over aromatic compounds
Corrosion inhibition	Salts (KCl)	low acute toxicity
	Polyglycols	low toxicity
	Silicate	low to moderate acute toxicity
	Polyacrylamides	different toxicological properties
pH control	NaOH, KOH	skin and eye irritation, corrosive
	$Ca(OH)_2$	may cause irritation
	Citric acid	low acute toxicity
	$NaHCO_3$	low acute toxicity
Other	Bactericides	different toxicological properties
	Lubricants	different toxicological properties
	Lost circulation material	dust hazard

When the drilling mud is brought to the surface, it brings drill cuttings with it. The drilling mud composition is complex and includes the base fluid, additives, and heavy metals from

the drilled rock. The solid and liquid percent of each waste are different and total petroleum hydrocarbons retained on the surface are reported to be 100,000 to 400,000 mg⁄kg.

2.4 History of waste drilling mud

Environmental problems associated with the waste drilling mud were recognized over 50 years ago, in the Gulf of Mexico in the 1970s (Wills, 2000). Oil discharges resulting from the use of non-aqueous drilling fluids were observed until 2000 when the strict Oslo and Paris convention (OSPAR) regulations came into effect (Wills, 2000). Since then, oil and gas exploration and production companies have been working towards zero discharge. In the United States, more than 25% of the produced drilling waste of land oil wells was disposed into the ocean in 1985, but this amount was reduced to only 3% in 1995. The use of oil-based fluids significantly decreased in the U.S. between 1985 and 1995 as listed in Table 2.4 (Dutton et al., 2000). The American Petroleum Institute (API) estimated that in 1995, about 150 million barrels of waste drilling mud were produced from the oil wells on land in the United States only (Haut, 2006).

Table 2.4 – Drilling waste by mud type in the United States (Dutton et al., 2000)

Year	Mud base			
	Freshwater	Saltwater	Oil	Other
1985	64%	23%	7%	6%
1995	92.5%	5.5%	<1.5%	0.5%

2.5 Environmental regulations applied to drilling waste

The United States Environment Protection Agency (USEPA) has developed strict regulations regarding drilling waste (Orszulic, 2008). For offshore drilling, the EPA's Effluent Limitation Guidelines (2000) set the retention on cuttings (ROC) of oil-based mud and cuttings to 0% (Al-Ansary and Al-Tabbaa, 2007). Compliance with the zero discharge policy have become a significant challenge for the oil and gas industry (Siddique et al., 2017). Waste drilling mud disposal, reuse, and/or treatment should be in accordance with local authorities' conditions (Zhang et al., 2016) many of which have their own regulation. For instance, for offshore drilling in the Gulf of Mexico, the "average" retention on cuttings for synthetic-based mud and cuttings must be 6.9% or less for ocean discharge (Childs et al., 2005). Under Oslo and Paris commission regulations, in the case of using oil-based mud, the standard of 1% drilling fluid on dry cuttings applies (OSPAR Commission, 2002). No oil-based mud discharges have been reported since 2004 (OSPAR Commission, 2009). Table 2.5 lists the local drilling mud and its cuttings disposal regulations in some of the most significant oil producers around the world. Newfoundland and Labrador follows the same guidelines as the federal Canadian regulations.

Table 2.5 – Summary of disposal regulations for waste drilling mud and cuttings around the world (Bernier et al., 2003)

Country	**Water-based mud**	**Oil-based mud**	**Synthetic-based mud**
Australia	Discharge allowed subject to 1% oil limit on fluids, including free oil and diesel oil, and 17% KCl content of muds for exploratory drilling	1% oil limit on cuttings retention Restriction on fluids with aromatics > 1%	Fluid retention is limited at 10% and the cuttings discharge will be determined by a case-by-case basis
Brazil	No specific regulation and current practice is to allow discharge	Discharge prohibited	Discharge approved on a case-by-case basis
Britain	Discharge allowed but needs pre-approval according to OSPAR protocols	Under OSPAR 2000/3, discharge is subject to a limit of 1% oil on cuttings	No discharge allowed except exceptional circumstances
Canada	2002 draft guidelines allow discharge of WBMs without restrictions but encourage operators to reduce the need for bulk disposal of drilling fluids	2002 draft guidelines require specific approval to use OBMs but if used, the targeted oil is less than 6.9% wet weight oil on cuttings.	2002 draft guidelines allow cuttings to be discharged after the treatment and the targeted oil on cuttings retention limit is less than 6.9% oil limit on cuttings (wet weight)
China	Discharge allowed	ND	Government encouraging the use of low toxicity fluid. Minor volumes, when recovery is not possible, may be discharged subject to an appropriate discharge fee
Iran	May be discharged but cannot “contain persistent systematic toxins”	No drilling cuttings should be discharged	ND

Nigeria	May be discharged but monitoring of drilling mud disposal sites is required	Oil on cuttings limited to 1% with 0% goal	Must be recovered but the oil on cuttings is limited to 5% or less for discharge
Norway	Discharge allowed but subject to pre-approval	Under OSPAR 2000/3, discharge is subject to a limit of 1% oil on cuttings	When allowed, the oil limit on cuttings is 8-18% depending on the case
Qatar	May be discharged but cannot "contain persistent systematic toxins"	Discharge forbidden	ND
Russia	Base case is zero discharge with discharges from exploratory drilling authorized on a case-by-case basis	Discharge strictly prohibited	ND
Saudi Arab	May be discharged but cannot "contain persistent systematic toxins"	No discharge is allowed	ND

ND: Not Determined

2.6 Current technologies

Various treatment technologies have been proposed to treat the waste drilling mud. The treatment methods can be divided into four main categories: chemical, physical, biological, and thermal methods.

2.6.1 Chemical techniques

These kinds of treatment technologies are employed to destroy the contaminants or convert them to harmless compounds commonly found in the nature (Manual EPA, 2004). The

most common chemical methods involve oxidants such as hydrogen peroxide, ozone, or potassium permanganate ($KMnO_4$). Hydrogen peroxide is particularly effective when it reacts with ferrous iron (Fe^{2+}) to produce Fenton's reagent. Ferrous iron can be available in solid structure or can be added with the hydrogen peroxide as a catalyst. When hydrogen peroxide reacts with the ferrous iron, hydroxyl radicals (OH°), ferric iron (Fe^{3+}), and hydroxyl ions (OH^-) are formed (Watts and Dilly, 1996).

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\circ} + OH^- + Fe^{3+} \qquad \text{Eq. I}$$

The hydroxyl radicals break the petroleum hydrocarbon bonds of common petroleum constituents such as benzene, xylene, and polycyclic aromatic hydrocarbons. The hydroxyl ions pose high oxidizing strengths, and react particularly with organic compounds. The overall end result of the process is outlined below (Watts and Dilly, 1996).

$$H_2O_2 + \text{organic matter} \rightarrow H_2O + CO_2 + O_2 \qquad \text{Eq. II}$$

Another chemical treatment option is to solidify/stabilize the hazardous waste to convert them into less toxic materials. Many reports have been published regarding adding some chemicals for drilling mud solidification such as lime, cement, and aluminium sulphate (Al-Ansary and Al-Tabbaa, 2007; Chen et al., 2014; Deuel and Holliday, 2001); however, there are several disadvantages reported such as the increase in waste volume, difficulty to implement, and the need for other chemical compounds (Hester and Harrison, 1997).

Two novel methods, including electro coagulation (EC) and electro-oxidation (EO), were tested for the waste drilling mud treatment by (Ighilahriz et al., 2013). A cell with an anode, cathode, and a current-producing oxidizer such as OH^-. The study reported the electro-coagulation was not successful for organic matter removal, but around 95% removal efficiency was obtained with electro-oxidation. While the electro coagulation has an acceptable processing time the electro-oxidation does not. The current efficiency decreases during the reaction, and other complexes can also be formed (Ighilahriz et al., 2013). A comparison of the discussed chemical methods is presented in Table 2.6.

Table 2.6 - Comparison of chemical treatment technologies for waste drilling mud

Chemical Treatment Technologies	**Advantages**	**Disadvantages**
Ozone/Fenton's oxidation	• Effective in acidic pH • Low processing times • Less sensitivity to external disturbances • Possibility for both "in situ" and "ex situ" implementation	• Expensive to implement • Not as effective in high alkaline drilling waste treatment
Solidification/Stabilization	• Effective • Produce less toxic waste • Product can be used for other purposes	• Waste volume increase • Other chemical compounds required • Difficult to implement
Electro-coagulation/oxidation	• Effective • No chemical compound required • Acceptable processing time	• Continuous current required (energy)

2.6.2 Biological treatment

Biotreatment technologies involve the use of micro–organisms to degrade or mineralise the organic contamination of the drill waste (Megharaj et al., 2011). Biotreatment is advantageous due to simplicity; however, approaches such as bioremediation and land farming require a large area of flat land as well as relatively high biodegradation time (Getliff et al., 2012). It is generally accepted that further investigations are required to enhance rates of biotreatment technologies. Factors that impact remediation rates include, temperature, pH and aerobic conditions, the composition of the organic contaminants, the type of the treatment in use, and nutrients (Megharaj et al., 2011). If all of these conditions are favourable to the process, the time of the treatment can be decreased from months or years to weeks. Bioremediation, vermiculture, biopile-based remediation, composting, and bioreactors have been reviewed (Ball et al., 2012). The drilling mud bio-treatment techniques were reviewed and it was concluded that they all possessed slow reaction rates (i.e. high processing times) which was considered their main disadvantage (Ball et al., 2012). Specifically, for waste drilling mud treatments, the most successful proposed methods were bioremediation, slurry bioreactors, and microorganism-enriched microbial consortiums (Megharaj et al., 2011).

A bioremediation was tried for a drilling mud-polluted site with a high concentration of total petroleum hydrocarbon up to 270,000 mg/kg (Rojas-Avelizapa et al., 2007). In the field tests, composting was performed in two biopiles, one amended (with nutrients to get a C/N/P ratio of 100/3/0.5 plus a bulking agent (straw) at a soil/straw ratio of 97/3) and one unamended. A bulking agent (straw) was also used at a soil/straw ratio of 97/3. After

180 days, the total petroleum hydrocarbon retained on the surface was greatly decreased, from 99,300 to 5,500 mg⁄kg for the amended biopile and to 22,900 for the unamended biopile. These results demonstrate that enhancing of petroleum hydrocarbon remediation from mud-polluted areas is possible by the addition of appropriate bulk agent(s), balancing the nutrimental status and the aeration improvement (Rojas-Avelizapa et al., 2007).

A slurry bioreactor was also tested to treat the barite-free waste drilling mud and monitor the effects of nutrients (Alavi et al., 2014). Indigenous bacteria isolated from abandoned sites were adapted to 20% (wt⁄wt.) oil-based drilling mud as a carbon source, and at best, were able to increase the total petroleum hydrocarbon removal efficiency of up to 92.5% after 21 days. Therefore, the slurry bioreactors could accelerate the biodegradation of total petroleum hydrocarbons and are able to reduce remediation time (Alavi et al., 2014).

A useful and efficient method was developed and was able to remove hydrocarbons from the waste drilling mud by the successive enrichment of indigenous microorganisms (Chang et al., 2014). The constructed active microbial consortium showed great stability and the process improved the degradation of the contaminating crude oil, which showed its great potential for drilling mud bioremediation. Various waste drilling mud samples were tested and proved that drilling mud samples with a higher ratio of aliphatic/aromatic hydrocarbons are more susceptible to biodegradation (Sliwka et al., 2012).

2.6.2.1 Biotreatment in the arctic environments

The possibility of drilling mud biotreatment in arctic environments was also evaluated and it was concluded that most of them are not suitable due to low temperatures and other climatic conditions (Eia and Hernandez, 2006). Land farming also requires agriculture land available all year with subsequent preferential temperature which is not available in the arctic environments, and biopiles, composting, or worm farming are all temperature sensitive.

2.6.3 Thermal treatment

Thermal technologies include a range of processes that remove or destroy hydrocarbon pollutants in the drilling waste by desorption, incineration, gasification, volatilization, and pyrolysis or a combination (Thanyamanta, 2003). For drilling mud treatment, three of these thermal treatments have been commercially tested, including incineration, thermal desorption, and thermal phase separation.

2.6.3.1 Incineration

Incineration is a process that uses high temperatures up to 1600°C to completely oxidize organic pollutants (up to 99%) (Thanyamanta, 2003). Incineration is considered an effective and fast method which destroys the solid particle structures and may remove all natural components and may produce toxic gases such as chlorine, NOx, and SOx which require further post-treatment processes (Ball et al., 2012). This high-temperature process

can be implemented both onshore and offshore (AEUB, 1996) and usually generates solid debris or ash which can later be landfilled (Cripps, 1998). Rotary Kilns are commercially available to incinerate the waste drilling cuttings and drilling mud. Rotary kilns can handle wastes with high hydrocarbon contents to less than 1% total petroleum hydrocarbon (TPH). Therefore, the waste drilling mud, high in hydrocarbon content, is particularly suited for incineration using rotary kilns (MI Swaco, 2016). Incineration efficiency decreases with water content.

2.6.3.2 Thermal desorption

Thermal desorption operates at temperatures up to 600°C to volatilize organic contaminants. Thermal desorption is a separation process which does not destroy organics like incineration (Thanyamata, 2003). Rotary dryers and thermal screws are the most commonly used thermal desorption equipment (Ball et al., 2012). Rotary dryers are the horizontal cylinders that are fired (directly or indirectly) and are usually inclined and rotated to increase the surface area contact. In thermal screw systems, the waste is transported through hollow augers and hot oil or steam circulates through the auger to indirectly heat the drilling waste. Similarly, rotary movement increases the surface area contact. Soils and drilling muds with an organic content of less than 2 wt.% are suitable for treatment with rotary dryers, while thermal screws can treat soils and drilling wastes with hydrocarbon content up to 50% (Noyes, 1998). Like incineration, the toxic gaseous

waste stream is produced requiring post-treatment technologies such as adsorption or fibre filtration.

2.6.3.3 Thermal phase separation (post-treatment technology)

In this post-treatment process, the produced gases are condensed and separated, so the heavier hydrocarbons can be recovered. Thermal phase separation has been reported to be efficient for different types of wastes, including petroleum pollutants such as drilling mud, drilling cuttings, sludge, and contaminated soils. This method is specifically suitable with wastes containing petroleum hydrocarbons up to 60% with solid particles less than 100 microns (Ball et al., 2012). Thermal phase separation has the ability to recover the contaminants from the drilling mud up to 99% without combustion. It can be considered a safe process with the recovery of oil with little fractioning or degradation, but the cost can be a challenge which is also greatly dependent on the type and quality of oil recovered from the process (Aird, 2008).

Thermal processes can reduce the waste volume by completely destroying the pollutants; however, cost, energy usage, and the production of other emissions such as toxic gases have limited their use. In addition, the wastes may need to be partially dried prior to treatment. Table 2.7 compares the main thermal processes in use for the waste drilling mud considering factors such as cost, efficiency, and environmental impacts (waste volume production and extra pollution caused). Although incineration is effective in oil removal,

its disadvantages have limited its applications. Other treatment methods may have lower environmental issues; however, all of them possess high energy and cost requirements.

Table 2.7 – Comparison of thermal treatment processes for waste drilling mud

Thermal Method	**Advantage(s)**	**Disadvantage(s)**
Incineration	Effective High waste volume reduction	Higher energy requirements and cost compared to other methods Hazardous gas production Destroys the solid particle structures Removes natural components
Thermal Desorption	Effective Suitable for highly polluted wastes (up to 50% hydrocarbons)	High energy requirements Relatively high cost Toxic gas production
Thermal Phase Separation	Effective No combustion No toxic gas production Recovery of heavier hydrocarbons Suitable for waste with up to 60% hydrocarbons Suitable for fine particles (less than 100 microns) Recovery of oil with little fractioning or degradation	Cost significantly varies by contamination type High energy requirements

ND: Not Determined, * Based on soil remediation investigations

2.6.4 Physical treatment

2.6.4.1 Centrifugal separation

Waste drilling mud is a solid-liquid mixture. Centrifugal separation has been widely accepted as a fast and efficient method for solid-liquid separation (Bobo and Hoch, 1954); however, the technology is less effective at removal of contaminants bound to the surface of the fine solid phase of the waste drilling mud. In addition, the centrifuge must be operated carefully as there is a risk of further dispersing fines into the liquid phase. As such, centrifuges could only be considered as a pre-treatment process to separate liquid from the solid phase.

2.6.4.2 Supercritical fluid extraction

Supercritical fluid extraction (SFE) has been tested for the removal of various forms of hydrocarbons from the waste drilling mud. In supercritical fluid extraction, a solvent is heated and compressed to above the critical temperature and critical pressure (Saldana et al., 2005). Supercritical fluids have liquid-like densities, gas-like viscosities, and zero surface tension as well as pressure-dependent solvating power (McHugh and Krukonis, 2013). The high diffusivity of the supercritical fluid extraction process can improve the mass transfer and generates a more rapid rate for hydrocarbon and oil removal and recovery from porous materials such as waste drilling mud (Lopez-Gomez, 2004). This method has several advantages over some common remediation technologies, including lower solvent usage, shorter extraction time and most notable, easy separation of pollutants from the

solvent by a slight change of temperature and/or pressure (Saldana et al., 2005). In contrast, there are some disadvantages that should be resolved to increase the application of this method for the waste drilling mud remediation. Depending on the type of solvent, there may be safety issues regarding the pressure and temperatures at critical conditions. It also requires high capital investment (Lopez-Gomez, 2004). Estimated total costs of this process are 148-447 USD per ton (Saldana et al., 2005). Carbon dioxide (CO_2) is the most widely used supercritical fluid due to its non-flammability and being chemically inert (Thanyamanta, 2003). Carbon dioxide is considered a non-toxic solvent with low adverse environmental impacts that possesses relatively low critical temperature and pressure (T_c = 31°C and P_c = 74 bar) (Saldana et al., 2005; Lopez-Gomez, 2004). It is also available in its high purity at a relatively low cost and it can be easily removed from the solid phase after the extraction process. Modifiers, normally solvents, such as methanol, toluene, and acetone, are added either directly to the solid phase before the supercritical extraction process, or added to the supercritical fluid using a separate modifier pump.

Various studies have been conducted to investigate the possibility of using the supercritical fluid extraction process for the drilling waste remediation. Propane and freon were tested to remove petroleum hydrocarbons from drilling waste cuttings and an oil removal efficiency above 95% was observed (Eldridge, 1996). Supercritical propane and butane were suitable for the removal of both synthetic and natural oil from the drill cuttings (Seaton and Hall, 2005). Supercritical water oxidation was conducted on the oil-based drill cuttings with a total organic carbon (TOC) removal efficiency of 89.2% in 10 minutes at 500°C (Chen et al., 2017). Degradation of petroleum hydrocarbons by supercritical water

oxidation was also studied by Yao et al. and more than 97% of alkanes could be removed at temperatures more than 475°C in more than 2 minutes (Yao et al., 2018). Carbon dioxide was tested as a supercritical fluid to treat drilling waste on a lab-scale system (Street and Guigard, 2006; Street et al., 2007). A synthetic-based mud was used in experiments and up to 97% removal of the petroleum hydrocarbons was achieved. A temperature and pressure of 40°C and 145 bar, mixing rate of 50 rpm, and supercritical carbon dioxide flow rate of 30-40 ml⁄min for 90 minutes were employed in the process. The authors used the same procedure for oil-based drilling mud waste and were able to achieve a 98.9% hydrocarbon removal efficiency using an additive (not outlined in the study). Another study showed that the supercritical CO_2 extraction could be effective in oil recovery from oil-based waste drilling cuttings (Saintpere and morillon-Jeanmaire, 2000). Optimum operating conditions were determined to be 35°C and 100 bar. The results showed no alteration of the base oil composition after the supercritical fluid extraction (SFE) process. Therefore, the recovered oil can be re-used without any additional treatment. In a separate study, supercritical CO_2 was tested to recover oil from the drilling waste cuttings with, at best, 49.1% oil recovery efficiency was achieved at 79.5°C and 200 bar (Goodarznia and Esmaeilzadeh, 2006). Despite effective waste remediation by supercritical fluid extraction, high capital and operating cost and lack of availability of any commercial plant (technical and economic challenges) have limited the use of this process. More investigation is required to ensure a more effective and cost-effective supercritical fulid extraction process can be implemented. Research on drilling mud treatment using supercritical fluid extraction are summarized in Table 2.8. Despite the research conducted on the application of supercritical fluid extraction on waste drilling mud treatment, there is no or little

research present on the synthetic-based waste drilling mud and the effect of supercritical CO2 extraction on the removal and recovery of different fractions of the petroleum hydrocarbons. The effect of temperature, pressure, contact time and their possible co-interactions are also missing from the literature. These gaps will be investigated in the current thesis.

Table 2.8 - Supercritical fluid extraction processes tested for waste drilling mud and cuttings

Supercritical Fluid	**Pressure (bar)**	**Temperature (°C)**	**Efficiency (%)**	**Reference**
HFC 134a and Propane	44.8	121	98	(Eldridge, 1996)
CO_2	100	35	95	(Saintpere and morillon-Jeanmaire, 2000)
CO_2	124	50	96	(Odusanya and Guigard, 2002)
Propane and Butane	34.5	23	96	(Seaton and Hall, 2005)
CO_2	145	40	98	(Street and Guigard, 2006; Street et al., 2007)
CO_2	200	79.5	49.1	Goodarznia and Esmaeilzadeh, 2006

2.6.4.3 Surfactant-enhanced washing

Surfactants are surface active compounds containing a hydrophilic head and a hydrophobic tail (Urum and Pekdemir, 2004; Urum et al., 2005) and are categorized, based on the net

charge of the hydrophilic head group, to anionic, cationic, non-ionic, and zwitterionic surfactants (Park and Bielefeldt, 2003). Surfactants possess specific physical properties such as solubility, surface tension, and critical micelle concentration (CMC) that can significantly affect surfactant-enhanced washing processes. Figure 2.4 illustrates how these physical properties typically change with increasing surfactant concentration. Critical micelle concentration, also known as CMC, is defined as the concentration at which the micelles is formed. CMC is the most important property of the surfactant and from an economic perspective, lower CMC values are desirable.

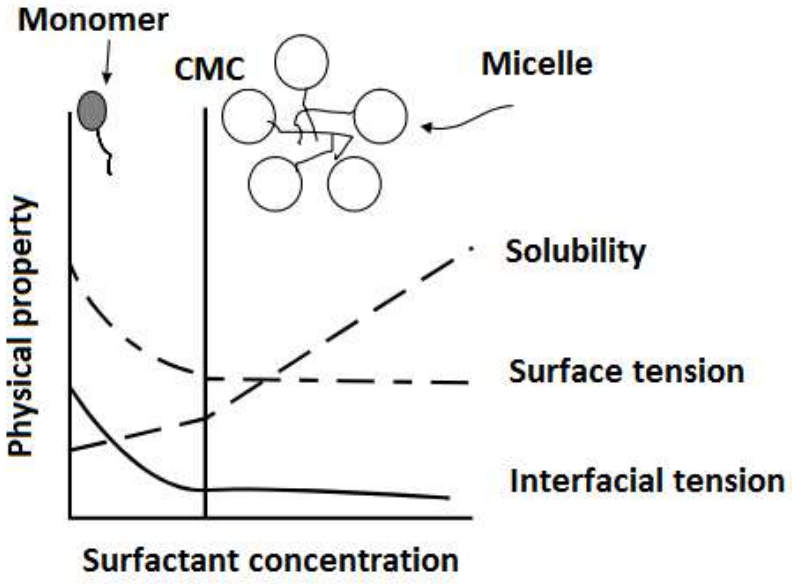


Fig. 2.4 – Surfactant properties with surfactant concentration (after Mulligan et al., 2001)

Generally, the removal mechanisms involved in surfactant-enhanced washing processes are categorized into three main streams: roll-up, snap-off or emulsification, and solubilisation mechanisms (Childs et al., 2005).

Roll-up involves the adsorption of the surfactant at the oil-water interface, thus increasing the contact angle between the oil and the solid phase (ɵ) and decreasing the interfacial tension between oil and water ($\gamma_{o/w}$). In this mechanism, oil can be removed from the surface with minimal mechanical agitation (energy). Figure 2.5 illustrates the roll-up mechanism. By adding a surfactant, the contact angle between the oil and the solid surface increases and thus, it would be easier to remove the entire oil droplet from the solid surface by mechanical agitation.

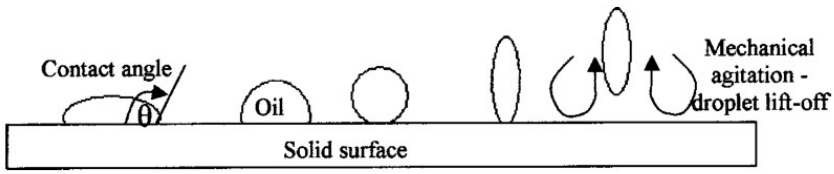


Fig. 2.5 – Roll-up mechanism for oil removal (after Childs et al., 2005)

Snap-off occurs when the contact angle is not high enough for the entire droplet to detach from the substrate, but a portion breaks off the deposited oil film, as shown in Figure 2.6. Interfacial tension of the oil portion and the water decreases in the presence of the surfactant and thus, a portion of the oil can be easily removed from the bulk using mechanical force. The snap-off mechanism is related to the interfacial tension, by the work

of cohesion (W_c), $W_c = 2\ \gamma_{o/w}$ (Childs et al., 2005). Similar to roll-up, the snap-off oil removal is facilitated by lower oil/water interfacial tension because less mechanical energy is required to overcome the work of cohesion of the oil.

Roll-up and snap-off mechanisms are desirable for oil removal as (i) the oil is liberated from the surface as a free phase top layer that can be skimmed from the bath, and (ii) they require low surfactant concentrations (less environmental risks and more economical feasibility). This mechanism happens in concentrations less than or slightly over the surfactant critical micelle concentration.

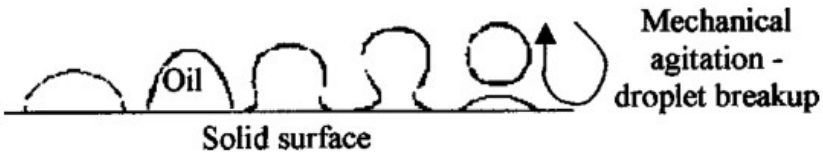


Fig. 2.6 – Snap-off mechanism for oil recovery from solid surface, also known as emulsification (after Childs et al., 2005)

Solubilisation mechanism is based on the partition of the oil molecules inside the hydrophobic core of micelles. This mechanism is only relevant at high surface concentrations when large numbers of micelles are present (Childs et al., 2005).

Surfactant-enhanced washing process has been considered an easy and cost-effective method (Chu, 2003; Han et al., 2009; Iturbe et al., 2004; Torres et al., 2005; Torres et al.,

2006; Zacarias-Salinas et al., 2013) which has widely been employed for drilling mud treatment. Experiments were conducted to test various surfactants and analyze their ability to treat oil-based drilling cuttings. Alfoterra 145-4PO, Dowfax 8390, Steol CS-330, Lubrizol, and Octyl sulfobetaine SB3-8 (lime soap dispersing agent, LSDA) were all tested for oil removal. The anionic surfactant, Alfoterra 145-4PO (the branched C14-C15 alcohol propoxylate sulfate), with additions of LSDA and Na_2SiO_3 showed the highest efficiency towards oil removal (Childs et al., 2005). The oil content was reduced to 4.7% by weight in 10 minutes, after which no further oil was removed. The surfactant concentration was reported to be 0.1% wt., and the addition of the modifier was reported to decrease the surfactant sorption into the solid particles. Surfactant loss was minimized and the oil removal was maximized using three components. More than 85% of the initial surfactant concentration remained in the bath after washing, which minimizes the need for make-up surfactant (Childs et al., 2005). It was also suggested that a combination of anionic and non-ionic surfactants could improve the washing properties over individual surfactants, as they usually form mixed-micelle aggregates that frequently exhibit properties remarkably different from those of the individual components as the ability of mixtures to solubilize oil can be greater than individual ones (Muherei and Junin, 2007). A commercial non-ionic surfactant to treat the drilling waste (containing 6-18% solid content) was employed in a mixture contained the non-ionic biosurfactant (Saponin), a coagulant (aluminum sulfate), a breaker (polyaluminum iron salt), petroleum ether, and two demulsifiers (Xie et al., 2013; Xie et al., 2014). Optimization of the entire process resulted in the maximum oil recovery of 95.2% and the wastewater produced was re-used in the process. The wastewater was used to dilute waste oil-based muds instead of freshwater. Results showed that the

wastewater could be re-used numerous times without affecting the oil removal efficiency (Xie et al., 2013; Xie et al., 2014). Similarly, a combined method of centrifuge and washing with chemicals were used to achieve an oil removal efficiency of 89.7% from the waste oil-based drilling mud. The optimum mixture was found to be 30% composite demulsifier (a mixture of two commercial demulsifiers, AP113 and SP169), 1.5% coagulant (Calcium Salt), and 0.1% flocculants (non-ionic polyacrylamide, industrial reagent) between 40-60°C (Guancheng et al., 2012).

Despite the various research reported on the use of different surfactants for the treatment of waste drilling mud, there is no or little research on the use of defined effective screening criteria for selection of the most suitable surfactant. Furthermore, there is barely any discussion on the sorption analysis and its impact on the waste drilling mud remediation by surfactant-enhanced washing. These gaps have been addressed in the current dissertation.

All the physical treatment technologies mentioned above have their own advantages and disadvantages/limitations and Table 2.9 compares reported methods in this chapter. The efficiency of these techniques may vary based on the type surfactants in use, waste type and its characteristics (such as contaminant concentrations, pH, density, and particle size distribution) and/or process operating conditions.

Table 2.9 – Comparison of physical treatment technologies for waste drilling mud

Physical Method	**Advantage(s)**	**Disadvantage(s)**
Centrifuge	Efficient in solid-liquid separation Fast	Inefficient in bound hydrocarbon removal High cost
Surfactant washing	Cost-effective Easy to implement	Increased waste volume
Supercritical fluid extraction	Efficient Less energy usage Less solvent required Short extraction times Easy to separate pollutants from the solvent	High cost Safety issues

2.7 Comparison of treatment technologies

Each of the discussed technologies possesses numerous advantages and limitations. Therefore, a detailed screening of these technologies considering their effectiveness, cost, and environmental impacts, is required before the development of an effective and environmentally-friendly process to treat the waste drilling mud.

Thermal treatment technologies are efficient but expensive methods to treat waste drilling mud (Hossain et al., 2013). In addition to their high cost, volatile heavy metals can be present in flue gases or accumulated on the treated solid surface (Thanyamanta, 2003; Bakhshian et al., 2009). Gases released into the environment such as NOx and SOx must be removed/reduced thereby adding capital and operational costs (Ball et al., 2012). High-temperature thermal treatment technologies may result in by-product compounds which may be more toxic or more volatile such as barium oxides or chloro-organic complexes.

Furthermore, recovery of drilling fluid for re-use is impossible due to the contaminant destruction. Other disadvantages of thermal methods include extra air pollution and the risk of fire hazard (Hossain et al., 2013). In spite of all these limitations and their high energy usage, their processing time is short for waste drilling mud and drilling cuttings remediation (Hossain et al., 2013).

Chemical treatment technologies do not normally have as high efficiencies as thermal technologies (Hossain et al., 2013); however, their capital costs are relatively lower as the major costs are chemical costs (Thanyamanta, 2003 and Hossain et al., 2013). The processing times for different chemical methods such as coagulation, chemical oxidation, and stabilization/solidification processes have been reported to be acceptable. Chemical technologies require little or no energy to be effective compared to other technologies (Hossain et al., 2013). Produced waste volume and mass, and the risk of environmental pollution are higher due to the use of additional chemicals and/or solvents such as chemical coagulants and solidified materials. These types of materials are hazardous and may pose serious environmental and health challenges (Hossain et al., 2013).

Physical treatment technologies do not require as much energy as thermal treatments and most of these treatment processes require shorter processing time compared to biological methods. Some of the methods are efficient but expensive in hydrocarbon removal, such as supercritical fluid extraction; however, others such as surfactant-enhanced washing are cost-effective and easy-to-implement processes with little energy requirement.

Biological methods, on the other hand, are typically successful in drilling cuttings and waste drilling mud (with fine particles) remediation with the least extra pollution

production among all other methods (Hossain et al., 2013) and low capital cost (Steliga et al., 2009); however, their energy requirements for process operation can be high, especially for arctic environments as the biological treatments and customized bioreactors are all temperature sensitive (Eia and Hernandez, 2006). Long processing time for drilling mud remediation using biological methods is the most difficult challenge to overcome for the implementation of such a technique (Ball et al., 2012). That is the main reason why bio-treatments must be improved to be considered feasible and easy to implement technologies.

2.8 Development and optimization of a treatment process

Various technologies have been employed for the waste drilling mud treatment. These technologies can be compared based on process efficiency and cost, environmental impact, processing time, and the physicochemical properties of the waste drilling mud. Figure 2.7 illustrates how a treatment process can be developed as a function of drilling mud properties and technological screening. For each proposed process, significant parameters should be identified and experimentally tested to determine their effect on process' efficiency, before the optimization of the remediation process is being conducted. The scale-up process should then be completed based on the experimental lab-scale results.

In the current research, two physical methods, surfactant-enhanced washing and supercritical CO_2 extraction, were selected based on their recovery efficiency, lower environmental impact, and low processing times. Little information is available on the selection of the surfactants for an effective sustainable surfactant-enhanced washing

process based on interfacial tension and sorption analyses, and comparison of these physical processes' efficiencies on the waste drilling mud remediation. Therefore, two physical treatment technologies were tested experimentally and the effect of significant parameters on each process was determined, and the optimization of the remediation process was also completed.

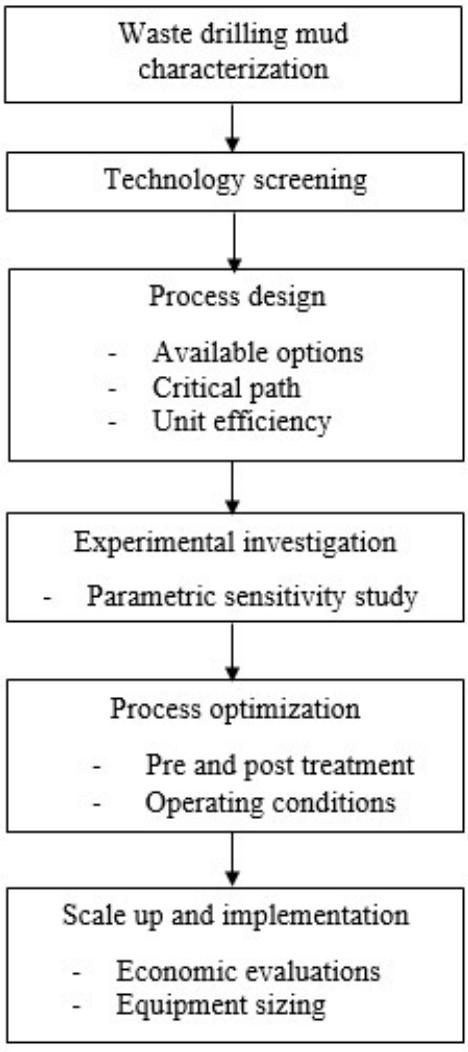


Fig. 2.7 – The process of developing a treatment process for waste drilling mud

2.9 Summary

In this chapter, the production, history, types and composition, relevant environmental regulations, and different treatment technologies of the waste drilling mud to meet the environmental and landfilling regulations, were all discussed. Removing petroleum hydrocarbons from the waste drilling mud can be a difficult task due to its complex structure and characteristics. Development and optimization of a sustainable and effective remediation process is required for the waste drilling mud to meet the strict landfilling regulations. Identifying such a process is challenging as it requires comprehensive knowledge on each treatment technology and how to optimize the remediation process based on significant parameters.

Since waste drilling mud and cuttings may contain other hazardous materials besides the petroleum hydrocarbons such as hazardous and/or heavy metals, detailed characterization of the waste is required to assess their presence and concentration (if present), and also to determine whether other treatments are required or not.

Comparison of the treatment technologies was conducted based on their efficiency, cost and energy requirements, processing time, safety issues, environmental impact, and their possibility of hydrocarbon separation and recovery. It was concluded that physical technologies are suitable candidates for the remediation of the waste drilling mud due to their relatively low processing times, low adverse environmental impacts, relatively low cost, high efficiencies, and the possibility of recovering petroleum hydrocarbons for re-use. Therefore, this research focuses on the selection of surfactants for the surfactant-enhanced washing process, and development and optimization of the surfactant-enhanced

washing and supercritical CO_2 extraction based on optimized operating conditions. The two processes will be compared for possible use to landfill the waste drilling mud.

Chapter 3: Waste Drilling Mud Characterization

3.1 Introduction

Waste drilling mud characterization is a key factor in determining the suitable treatment technology. Treatment technologies are chosen based on the phase and composition of the mixture, density and viscosity of the phase, contaminant concentration, pH, and particle size distribution of the solid. The composition of the waste drilling mud is also significant considering the strict environmental regulations to determine whether the waste drilling mud requires treatment and how such a treatment process should be developed. In the current chapter, characterization techniques to identify the composition and other properties of the waste drilling mud are discussed and the results of characterization analyses are listed.

3.2 Materials and methods

Since characterizations of the waste drilling mud may change the suitability and efficiency of treatments processes such as surfactant-enhanced washing and supercritical CO_2 extraction, complete characterization of the waste is a significant step to complete. Various tests were conducted to measure different properties of the waste drilling mud. In this section, these methods are discussed in detail and the materials, chemicals and their manufacturers, and equipment employed in the methods are listed.

Petroleum hydrocarbon concentrations were determined using the Tier 1 method which is the Canada-wide standard for petroleum hydrocarbons (CCME, 2007). Different petroleum hydrocarbon concentration ranges, C10-C16, C16-C34, and C34-C50, were determined. Details are also provided how the "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" were employed to measure the hazardous metal concentrations of the waste drilling mud (F. R. 11798, 1990). Details are also provided below on other characterization tests, their equipment, and procedure such as X-ray diffraction and scanning electron microscopy analyses.

3.2.1 Chemicals and equipment

Waste drilling mud used in this study was an industrially-generated synthetic based waste and came from the offshore production facilities in Newfoundland and Labrador. Carbon disulfide (CS_2) was used as the blank liquid solution for the petroleum hydrocarbon determination analysis (gas chromatography) and was supplied by Sigma Aldrich Co. (USA). Sodium sulphate was also provided by Sigma Aldrich Co. (USA). Calibration samples were provided by Supelco Canada Ltd. containing a hydrocarbon mix dissolved in Cyclohexane, listed in Table 3.1. Silica gel, methanol, acetone, and hexane were all supplied by Fisher Scientific, Canada. Diatomaceous earth was provided by Acros Organics; toluene was supplied by EMD Millipore; and dichloromethane (DCM) was a product of ACP, Canada. The waste drilling mud was provided by Environmental Universal Limited. For leaching experiments and for preparing the aqua regia solutions, hydrochloric acid (36.5-38%) and concentrated nitric acid (68-70%) were used as supplied

by ACP, Canada. All chemicals used in this study were American Chemical Society (ACS) grade.

Table 3.1 – Hydrocarbon mix of the calibration sample

Analyte	**Purity (%)**	**Weight concentration (µg/mL)**
N-Decane (C10)	99.9 %	1000
N-Hexadecane (C16)	99.9 %	1001
N-Tetratriacontane (C34)	99.9 %	1001
Pentacontane (C50)	99.9 %	1001

Multi-layer Millipore filters (0.45 µm) and 10 ml syringes were used for filtration before gas chromatography analysis and were sourced from Fisher Scientific Canada. A gas chromatograph (GC) equipped with a flame ionization detector (FID) and an auto-injector (Agilent 7890A) was used for the determination of the hydrocarbon fraction concentrations. A Pyrex glass soxhlet apparatus with a Glass-Col heater (179982A) was also employed in the hydrocarbon determination procedure.

The rotary evaporator employed in the hydrocarbon determination procedure is supplied by Buchi® (Model: R-210) with a water bath. Particle size distribution analysis was also completed after contaminant removal using a laser scattering particle size distribution analyzer (LA-950, HORIBA Scientific).

A Perkin-Elmer optimum 5300 DV inductively coupled plasma optical emission spectrometer (using the WinLab 32 software) with a Cetac ASX-520 Auto-sampler was employed for determining the metal concentrations in the leachate solutions. A Qcond 2200 conductivity meter from VWR International was employed to measure the electrical conductivity of the solution and an UP-5 pH meter, manufactured by Denver Instruments, was used to estimate the pH of the waste drilling mud.

A Rigaku Ultima-IV powder facility with a Copper source (40KV, 44mA) was employed for the X-ray diffraction analysis. The moisture content was also determined using Mettler Toledo – HB43-S equipment. A scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analyses were completed using a Quanta 400, FEI to obtain information about waste drilling mud surface topography and composition. The precision of EDX for major elements is generally around 2% and the limit of detection of EDX detectors are around 0.1 wt.%. An automated three-station TriStar II Plus surface area and porosity analyzer was employed to determine the BET surface area of the waste drilling mud.

3.2.2 Determination of petroleum hydrocarbon concentrations

The hydrocarbon fractions concentrations of the waste drilling mud were measured using the Tier 1 method both before and after each treatment process (CCME, 2007). Tier 1 is not a suitable method to determine the quantity of every individual hydrocarbon; however, it is recommended to be the appropriate method to measure the petroleum hydrocarbon

content for soil and sediment (CCME, 2007). Tier 1, the Canada-wide standard for petroleum hydrocarbons, is also accurate for crude oil contaminated sites or for most contaminated sites where refined products were discharged (CCME, 2007). The concentration of different hydrocarbon fractions and total petroleum hydrocarbons of the waste drilling mud before and after its treatment help to determine the removal efficiencies of the treatment processes. Hydrocarbon fractions were measured based on the results from the gas chromatography.

The C6-C10 hydrocarbon concentrations were not determined in this study as they are quickly vaporized and are typically destroyed while drilling processes are in operation and could not be measured as a part of the petroleum hydrocarbons available in the waste drilling mud and cuttings (Lopez-Gomez, 2004). For C10-C50 hydrocarbon concentrations, five grams of solid drilling mud was weighed and sufficient diatomaceous earth was used for drying. A soxhlet extractor, illustrated in Figure 3.1, was set up and 80 cc of hexane was mixed with 80 cc acetone (50:50) at a ratio of 32:1 solvent: dry soil ratio to wash the waste drilling mud. The time between two cycles was measured to be between 10-15 minutes (6-8 cycles per hour). The soxhlet extraction was performed for 22 hours (Tier 1 standard time is defined to be 21 to 24 hours).

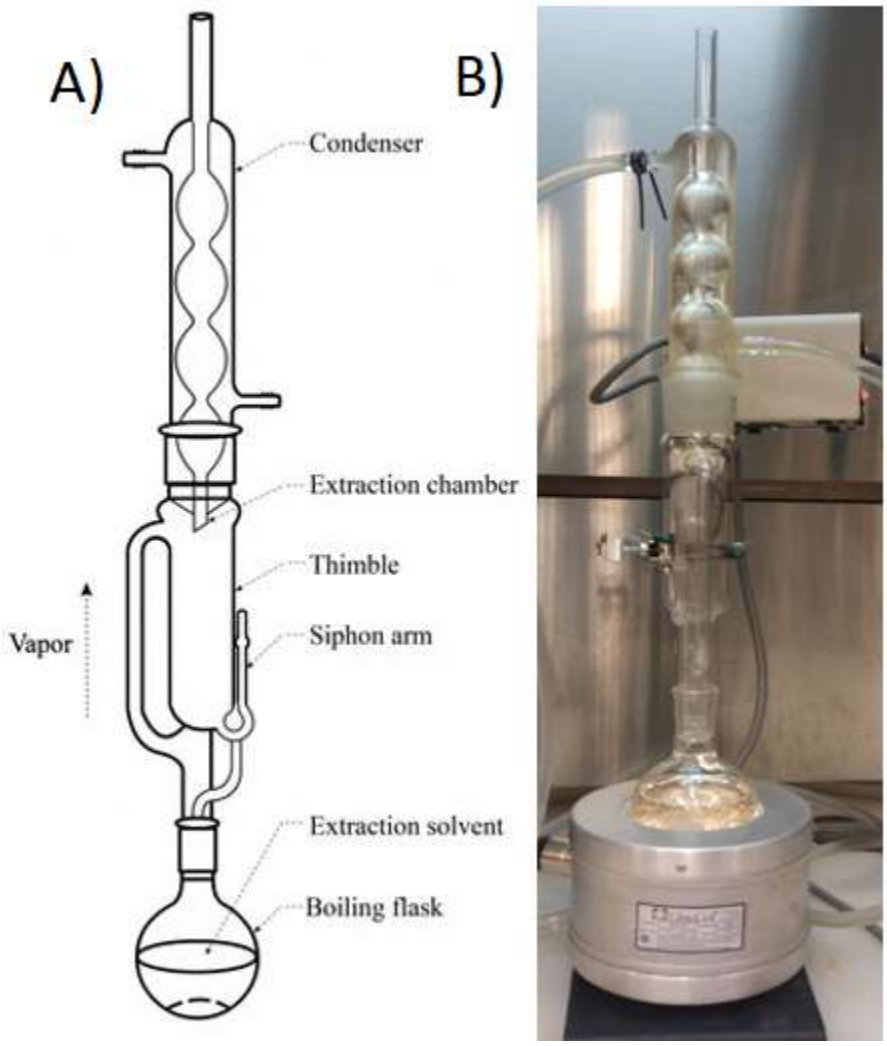


Fig. 3.1 – a) Schematic of pyrex glass soxhlet apparatus (after Sharang Scientific, 2016) and b) Soxhlet extractor in Hibernian EOR laboratory for hydrocarbon extraction from the waste drilling mud

The solvent was recovered and passed through 8-9g of dried sodium sulphate in a column. The sodium sulphate was used as a drying agent to remove any possible water from the solution. The column was then rinsed with 5-10 ml of hexane. Thereafter, 2 ml of toluene

was added and evaporation was completed in a rotary evaporator. Toluene was added because of its relatively high boiling point and when the evaporation was complete, the toluene remains with C10-C50 hydrocarbons. The temperature was set to be between 50 and 60°C to avoid losing nC10 hydrocarbons. The rotary evaporation process only took 10-15 minutes to obtain 1-2 ml of the remaining liquid. Then 20 mL of 50:50 n-hexane: dichloromethane was added to the recovered solvent. Three grams activated silica gel was added to the solution and the solvent was recovered after stirring for five minutes. Finally, 2 mL of toluene was added to the recovered solvent in an evaporating vessel and the operation conditions were similar to the previous rotary evaporation, until a 1-2 ml of the solvent solution was recovered and sent to gas chromatography for analysis. The details of the preparation and calculation are also listed in detail elsewhere (CCME, 2007). The rotary evaporator employed for the hydrocarbon concentration analysis is illustrated in Figure 3.2.

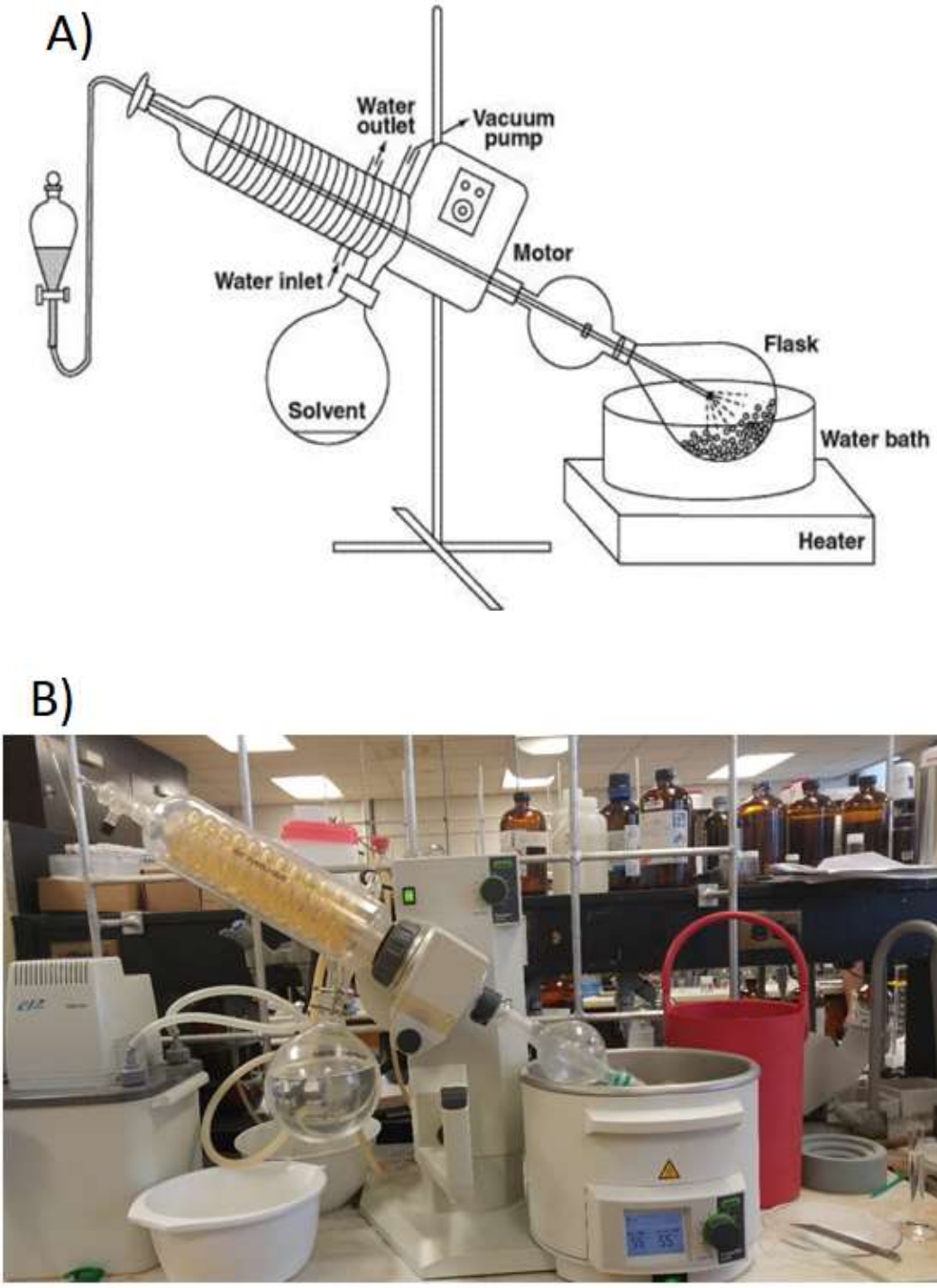


Fig. 3.2 – a) Schematic of a rotary evaporator (after Patel, 2013) and b) The actual rotary evaporator employed for hydrocarbon analysis

3.2.3 Determination of hazardous metal concentrations

Various hazardous metal concentrations were determined using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The reference method (leaching procedure) used to measure the toxicity of the waste drilling mud is Method 1113 of "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (F. R. 11798, 1990). According to the U.S. Environmental Protection Agency (EPA), a solid waste exhibits the characteristics of toxicity if the concentrations of the specific metals are equal to or more than the concentration listed in Table 1 of 40 CFR 261.24 method (F. R. 11798, 1990).

This method suggests the dissolution of the solid waste into a leaching agent with 20 times greater volume than the solid. Therefore, 5 g of the waste drilling mud was dissolved in 100 ml of aqua regia (hydrochloric acid 3:1 nitric acid) at ambient temperature and stirred for 24 hours using a magnetic shaker. The liquid phase was separated from the solid residue by vacuum ceramic filters. Four samples were submitted to an inductively coupled plasma optical emission spectrometer to measure the metal concentrations in the aqueous phases.

3.2.4 Acidity and particle size

The acidity of soil and sediment is a significant parameter as it is directly related to the soil ion exchange capacity, organic content, and clay mineralogy (Mirsal, 2008). Furthermore, it is a function of the adsorbed metals on the surface and their availability for extraction (Mirsal, 2008). The electrical conductivity and the pH of the waste drilling mud were

measured in 1:10 dry mud:water (g/ml) suspensions using a digital pH meter and an electric conductivity meter, respectively.

Particle size analysis was completed after contaminant removal using a laser scattering particle size distribution analyzer to obtain an accurate particle size distribution. Dispersion of the drilling mud was conducted to prepare the samples for grain size analysis by washing the sample with alcohol and acetone (Appendix I). X-ray diffraction analysis was also completed after sample drying to determine the mineral composition of the waste drilling mud sample, as it may help the selection of the most appropriate surfactant (Battelle, 2002).

3.2.5 Quality assurance and quality control (QAQC)

Various steps were taken to ensure all the experimental results presented in the current study are reliable, accurate, and reproducible. Detailed methodologies and steps followed for all experimental tests were recorded and presented in the thesis. 3-point calibration of the facilities used in the enhanced oil recovery laboratory was completed before the experimental tests. All the experimental results are presented as the average of at least triplicated experiments to ensure the results are valid and reliable and the error is kept at the minimum. Laboratory experiments including experiments from the designed matrix for supercritical CO_2 extraction were randomly conducted to minimize error and to avoid or minimize the effects of uncontrolled factors. All these steps resulted in dependable and accurate results.

3.3 Results and discussion

The properties of the waste drilling mud can significantly affect the efficiency of the surfactant-enhanced washing and supercritical CO_2 extraction processes. These factors include, but are not limited to, pH, composition, cation exchange capacity (CEC), particle size distribution, permeability, and types of contaminants on the solid surface (Mulligan et al., 2001). The characterization of the waste drilling mud is listed in Table 3.2. Solid particle size analysis was conducted for 10 samples to achieve consistent data and the average amounts are presented. All other analyses, such as pH and moisture content tests were conducted four times and the average values are presented in Table 3.2. The solid surface charge is more negative at higher pH values (Bohn et al., 2015; Paria and Khilar, 2004; Farn, 2008). The pH was measured to be approximately nine, hence the surface charge is expected to be negative. This finding shows that cationic surfactants have high potentials for adsorption to the waste drilling mud sample while anionic surfactants are less likely to face loss.

Table 3.2 – Waste drilling mud sample characterization

Characteristic	**Value**
Moisture (%)	13.49 ± 0.77
Solid percent (mass/mass %)	97 ± 1
pH	8.96 ± 0.26
Electrical conductivity (μS)	839 ± 9

Density g/cm^3		1.97 ± 0.20
Solid particle size	Average mean size (µm)	25.62 ± 5.47
	Average median size (µm)	16.92 ± 2.22
BET surface area (m^2/g)		1.92 ± 0.26
C10-C16 hydrocarbons (mg/kg)		65,298 ± 470
C16-C34 hydrocarbons (mg/kg)		34,320 ± 613
C34-C50 hydrocarbons (mg/kg)		1,800 ± 300
Total petroleum hydrocarbons (mg/kg)		101,418 ± 478

Figure 3.3 illustrates the particle size distribution of the waste drilling mud solid particles before any processing or treatment. The y-axis is the % by volume of the corresponding particle size shown on the x-axis. This distribution shows the pattern of fine particles for the waste drilling mud sample.

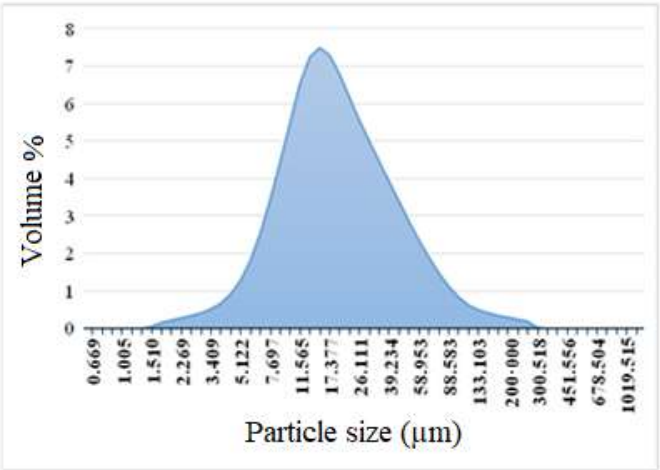


Fig. 3.3 – Particle size distribution of the waste drilling mud before any treatment or processing

Table 3.3 lists the average results and the limits of the Environmental Protection Agency and the Government of Newfoundland and Labrador for hazardous metal concentrations. It can be implied from Table 3.3 that all the metal concentrations are below the limit required by landfilling regulations. Therefore, the waste drilling mud could be landfilled if the petroleum hydrocarbon concentration is reduced to meet the maximum hydrocarbon concentration permitted by regulatory agencies.

Table 3.3 – ICP-OES analysis results and applicable regulations on hazardous metal concentrations

Metal (mg/l)	**Pb**	**Cd**	**Cr**	**As**	**Ba**
Metal concentration	3.78 ± 0.41	<0.01	0.43 ± 0.10	0.24 ± 0.03	29.74 ± 11.47
U.S. EPA limit (F. R. 11798, 1990)	5.00	1.00	5.00	5.00	100.00
Newfoundland Limit (Ryan, 2003)	5.00	0.50	5.00	2.5	100.00

X-ray diffraction analysis was completed to determine the composition of the waste drilling mud. The results are illustrated in Figure 3.4. Two different samples of the waste drilling mud generated almost identical results implying that the waste drilling mud was homogenous. Compounds were identified by matching the peaks positions and intensities to the database software. The results showed that calcite ($CaCO_3$), barite ($BaSO_4$), and quartz (SiO_2) are the three most abundant minerals in the waste drilling mud with the normalized percentages of 77.1% (±5%), 12.7% (±0.8%), and 10.2% (±0.7%) respectively.

$CaMg(CO_3)_2$, also known as dolomite, may also be present in the sample; however, its quantity was measured to be below the detection limits. The abundance of calcite in the sample typically generates an alkaline pH (Chesworth et al., 2008) as observed in Table 3.2, to which the negative charge of the surface can be attributed.

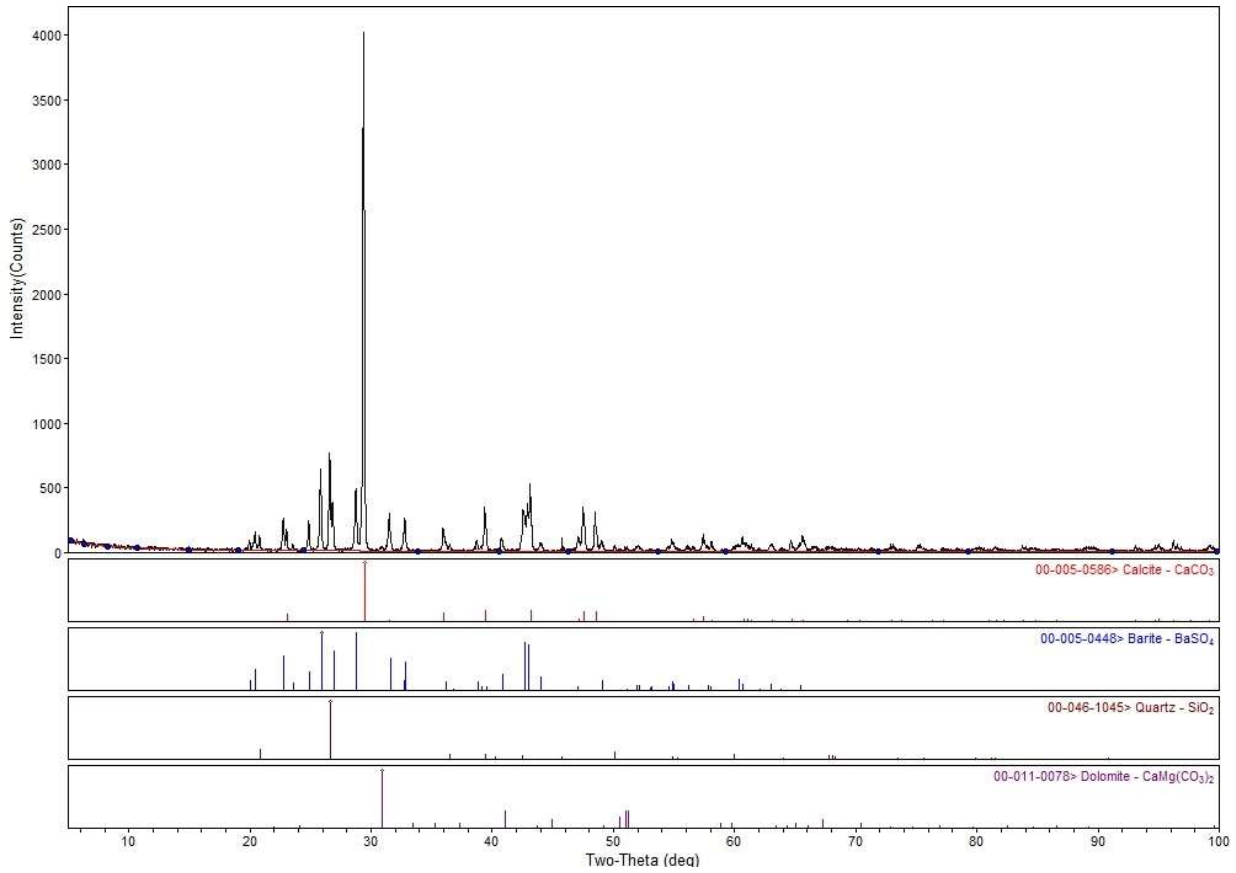
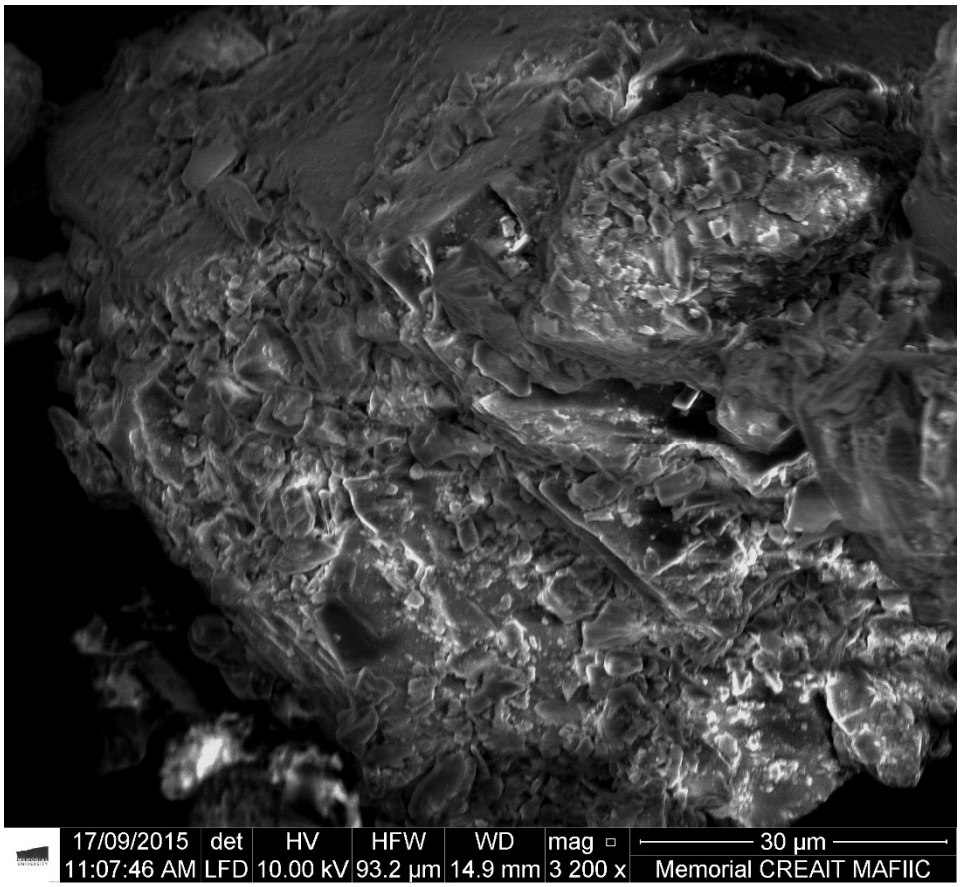


Fig. 3.4 – X-ray diffraction results for the waste drilling mud

SEM and EDX analyses were completed to determine the topography and composition of the waste drilling mud surface. The porous surface of the waste drilling mud and the

qualitative analysis of the surface composition are illustrated in Figures 3.5. The results agree with previous analyses as calcium, barium, sulfur, and silicon are abundant in the sample.



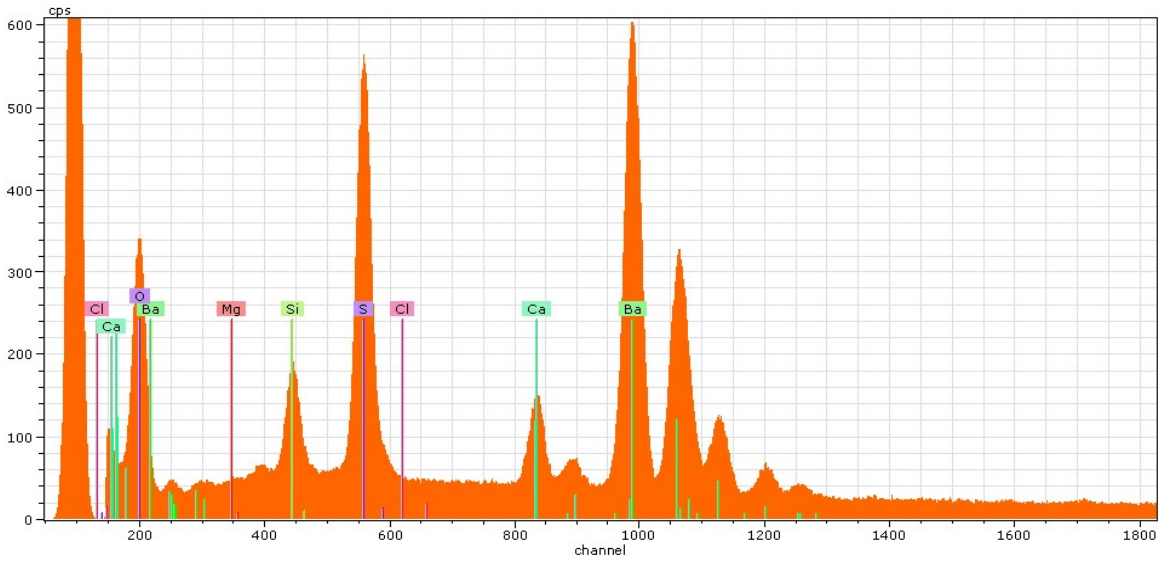


Fig. 3.5. Scanning electron microscope (SEM) and the energy dispersive X-ray spectroscopy (EDX) analyses for the waste drilling mud

3.4 Summary and conclusions

The results of the characterization analyses for the waste drilling mud showed that our sample is heavily contaminated with total petroleum hydrocarbon concentration of near 100,000 mg/kg and possesses a negative surface which will help us employ the appropriate types of surfactants (discussed in Chapter 4). Waste drilling mud is also highly alkaline and has an average mean size of 25.62 ± 5.47 μm. Our waste drilling mud mostly contain calcite ($CaCO_3$), barite ($BaSO_4$), and quartz (SiO_2). The high concentration of petroleum hydrocarbons in the sample shows that the drilling mud requires efficient treatment; however, the hazardous metal concentrations in the sample are lower than the regulatory limits and thus, the waste drilling mud do not require any further treatment for the hazardous metals to meet the landfilling requirements.

Chapter 4: Surfactant Selection; Evaluation and Development of a Surfactant-enhanced Washing Process to Treat the Waste Drilling Mud

4.1 Introduction

In this chapter, two different analyses were employed to determine the most suitable surfactant for the surfactant-enhanced washing (SEW) of the waste drilling mud. Interfacial tension and sorption analyses were used to analyze three surfactants: one anionic (Alfoterra 145-8S 90), one non-ionic (Triton 100), and one non-ionic biosurfactant (Saponin). Details of the procedures and how the analyses were conducted are discussed in this chapter. After the surfactant selection, significant factors for the surfactant-enhanced washing were determined and the experiments were conducted to investigate the effects of these parameters on the process' petroleum hydrocarbon removal efficiencies. The optimized operating conditions were also determined at the end of the chapter.

4.2 Surfactant selection strategy

Cationic surfactants have rarely been employed for soil, sediment, and drilling mud treatment due to their hazardous nature to humans and the environment and their high potential of sorption to solid particles (Mulligan et al., 2001; Kim and Lee, 2000). Anionic surfactants have lower toxicity than cationic ones; however, their toxicity may still limit their application in organic pollutant removal from solid particles. They typically possess

critical micelle concentrations (CMC) higher than those of cationic and non-ionic surfactants, so they should be prepared at higher solution concentrations (Kim and Lee, 2000). Despite these disadvantages, anionic surfactants have the least potential for sorption to solid particles, which is one of the reasons various studies have investigated their effect in organic contaminants removal from solids. Non-ionic surfactants are considered excellent candidates for surfactant-enhanced washing processes due to their intermediate sorption and low biotoxicity. They also do not react with multivalent cations (Mulligan et al., 2001; Kim and Lee, 2000). Another reason why non-ionic surfactants are usually considered for the surfactant-enhanced washing processes is that their critical micelle concentrations are typically much lower than that of ionic surfactants and a larger fraction of the surfactant is in micellar form causing their high effectiveness in solubilizing organic pollutants (Singh and John, 2013). Non-ionic surfactants can be used in mixtures and/or with additives such as alcohol and/or salts such as sodium chloride. These agents would be most effective in promoting the mobilization of organic compounds with relatively low water and high lipid solubilities. Non-ionic biosurfactants can also be considered effective and environmentally-friendly surfactants for surfactant-enhanced washing processes due to their low sorption to solids, biodegradability, low toxicity, better environmental compatibility, and high activity at extreme temperatures and salinity (Wang and Mulligan, 2004). Due to their physico-chemical characteristics, they are expected to be more effective than synthetic surfactants and can be blended with other (bio and/or synthetic) surfactants to offer desirable performance characteristics (Kaloorazi and Choobari, 2013). In some cases, a mixture of surfactants with lower critical micelle concentrations has been found

more useful for organic matter removal from contaminated soil and sediments (Wang and Mulligan, 2004).

The interfacial tension of oil/aqueous phases typically decreases in the presence of a surfactant and the lower interfacial tension corresponds to more complete remediation, as illustrated in Figure 4.1. Therefore, the interfacial tension analysis can be considered a screening test for the surfactant selection.

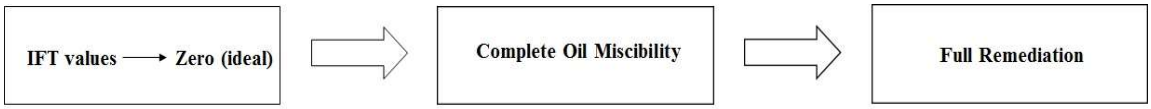


Fig. 4.1 – Relation between lower interfacial tension and remediation capabilities of surfactants

Sorption of the surfactant into the solid particles may result in surfactant loss and reduced performance for the removal of contaminants from soil, sediments, and waste drilling mud (Chu and Chan, 2003). The amount of surfactant loss may be affected by several parameters, including possible electrostatic attraction, covalent bonding, and hydrophobic bonding between the surfactant and the solid surface (Paria and Khilar, 2004). Therefore, sorption analysis can also be employed in parallel with the interfacial tension analysis to select the most suitable surfactant for the surfactant-enhanced washing of the waste drilling mud.

4.3 Materials and methods

Interfacial tension analysis was employed as the screening method for selection of the most suitable surfactant for the surfactant-enhanced washing of the waste drilling mud and the washing experiments were conducted to determine the effect of three different parameters. In this section, the chemicals and equipment employed for the interfacial tension analysis and surfactant-enhanced washing are listed and the methods and procedures followed are discussed. Details are provided on how the experiments and different analyses were conducted that ensure the reproducibility of the results.

4.3.1 Selected surfactants for the surfactant-enhanced washing process

Three surfactants were selected from the literature due to their potential for waste remediation (low interfacial tension) and their low sorption to solid particles. They are listed in Table 4.1.

Table 4.1 – Three surfactants used in this study; Triton 100, Alfoterra 145-8S 90, and Saponin

Surfactant	**Provider**	**Type**	**State**
Triton 100	Fisher Scientific	Non-ionic	Liquid
Alfoterra 145-8S 90	Sasol Inc.	Anionic	Liquid
Saponin	Acros Organics	Non-ionic biosurfactant	Solid

Triton 100 (TX-100) is a non-ionic surfactant and has previously been tested for the petroleum hydrocarbon removal and is capable of achieving an efficiency of 90% for specific hydrophobic compounds in the presence of sodium dodecyl sulphate (SDS) as an additive (Zhong-Yi et al., 2014). Saponin is a non-ionic biosurfactant which possesses excellent physiochemical and biological properties with an elemental analysis of 51% oxygen, 42-44% carbon, and 6-6.2% hydrogen (Khan et al., 2011). The lipid-soluble aglycone (hydrophobic scaffold) and several hydrophilic oligosaccharide chains present in the structure of Saponin (Golemanov et al., 2014) (amphiphilic nature) make it a unique surfactant because of its wetting, foaming, and emulsifying properties (Guclu-Ustundag and Mazza, 2007). Saponin has proven to be effective for both hydrophobic organic compounds (HOCs) and heavy metals. Heavy metals tend to form stable complexes with Saponin and 90% removal efficiency could be achieved using Saponin (Xia and Yan, 2010). Figures 4.2 and 4.3 illustrate the chemical compositions of Triton 100 and Saponin. Alfoterra surfactants, illustrated in Figure 4.4, are a series of anionic surfactants with excellent abilities to reduce the interfacial tension between oil and water, and can improve oil separation from the contaminated solids. In this study, Alfoterra 145-4S 90, a C14-15 branched and linear, propoxylated, sulphated, sodium salt, was tested to reduce the interfacial tension between oil and the water. In a similar approach, Alfoterra 145-4PO was successfully employed for oil removal from the waste drilling cuttings (Childs et al., 2005). Sodium dodecyl sulphate, illustrated in Figure 4.5, is an anionic surfactant which has been employed as an additive in this study.

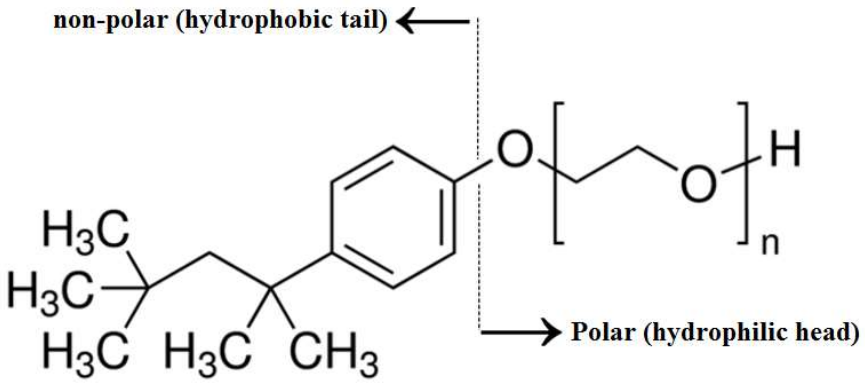


Fig. 4.2 – Chemical structure of Triton 100 (Fisher Scientific, 2014)

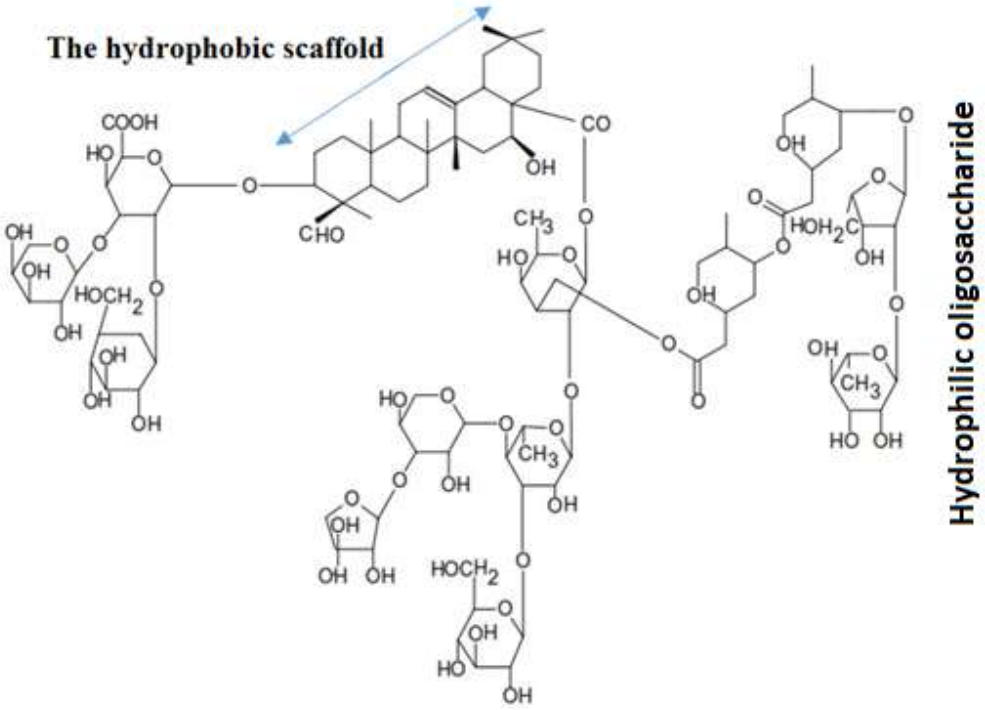


Fig. 4.3 – Chemical structure of Saponin (Fisher Scientific, 2018)

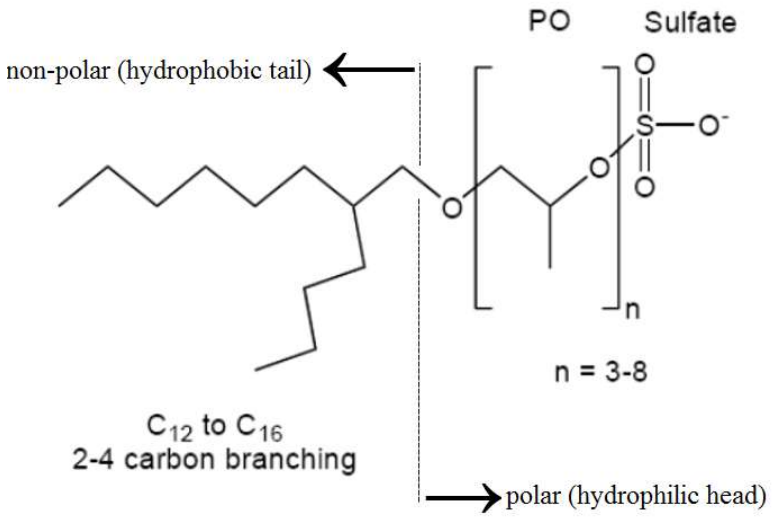


Fig. 4.4 – Chemical structure of Alfoterra surfactants (Gupta, 2016)

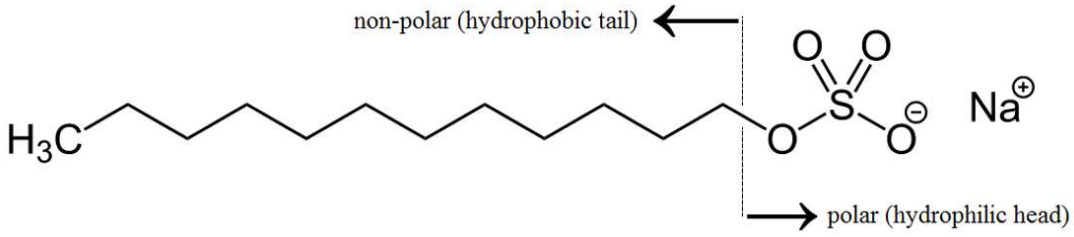


Fig. 4.5 – Chemical structure of sodium dodecyl sulphate, used as an additive (Sigma-Aldrich, 2018)

Alfoterra 145-8S 90 was supplied by Sasol Inc. and Triton 100 was provided by Fisher Scientific, Canada. Mercury Chloride, employed in the sorption analysis, and Saponin were both supplied by Acros Organics. Sodium dodecyl sulphate was provided from EMD

Millipore. The waste drilling mud was provided by Environmental Universal Ltd. and all other chemicals were used as received. The base oil of synthetic drilling fluid was used for the interfacial tension measurements and was provided by MI SWACO, A Schlumberger Company. The interfacial tension analysis was completed using the interfacial tension meter, IFT 700, Vinci Technologies, France (temperature accuracy of 0.1°C). A Sorvall ST 16 centrifuge, manufactured by Thermo Scientific, was also employed for centrifugation.

4.3.2 Interfacial tension measurements

The Pendant Bubble method was used to measure the interfacial tension between the surfactant solutions and oil. Diluted surfactant solutions with deionized water were prepared at wt.% concentrations of 0.1%, 0.25%, 1.25%, 2.5%, and 5%. Deionized water was used to dilute the surfactant solutions and the interfacial tension diagrams were plotted against each other. Interfacial tension analysis is an excellent screening test as lower interfacial tensions correspond to more complete remediation. Interfacial tension values for 0.1 wt.% and 5 wt.% were measured at 22°C, 30°C, and 40°C to analyze the effect of temperature on the surfactants' abilities to reduce the interfacial tension. All experiments were conducted in duplicate to ensure the repeatability of our experiments. In many cases, synergic behaviour of mixed surfactants showed better solubilization and surface tension lowering (Shi et al., 2015); therefore, the effect of sodium dodecyl sulphate on the interfacial tension was also calculated.

4.3.3 Sorption analysis

Sorption of the surfactant may result in surfactant loss and reduced performance for the contaminant removal from soil, sediments, and waste drilling mud (Chu and Chan, 2003). The amount of surfactant loss may be affected by several parameters including possible electrostatic attraction, covalent bonding, and hydrophobic bonding between the surfactant and the solid particles (Paria and Khilar, 2004). In this study, interfacial tension analysis with the base oil of synthetic drilling fluid was employed to investigate the loss of surfactant due to sorption into the waste drilling mud solid particles. In our experiments, the interfacial tension between the three surfactants (Alfoterra 145-8S 90, Saponin, and Triton 100) and the base oil of synthetic drilling fluid was measured in different surfactant concentrations for the fresh surfactant solutions and the mud-surfactant solutions supernatants. The two measurements were plotted at the same scale. Any arbitrary point on the interfacial tension axis can be selected to intersect with the pure surfactant line to provide a monomer surfactant concentration (section A). A higher surfactant concentration is required to reach the same interfacial tension in the surfactant mixed with drilling mud system. The difference between these surfactant concentrations (section B) identifies the amount of surfactant sorption to the waste drilling mud (Figure 4.6). The minimum interfacial tension of both systems can be identified in the inflection points of both curves. That is where the bulk solutions are saturated with surfactant monomers. Once the saturated point is reached and the interfacial tension is at its minimum, no more surfactant loss is observed due to a lack of sorption sites (Chu and So, 2001).

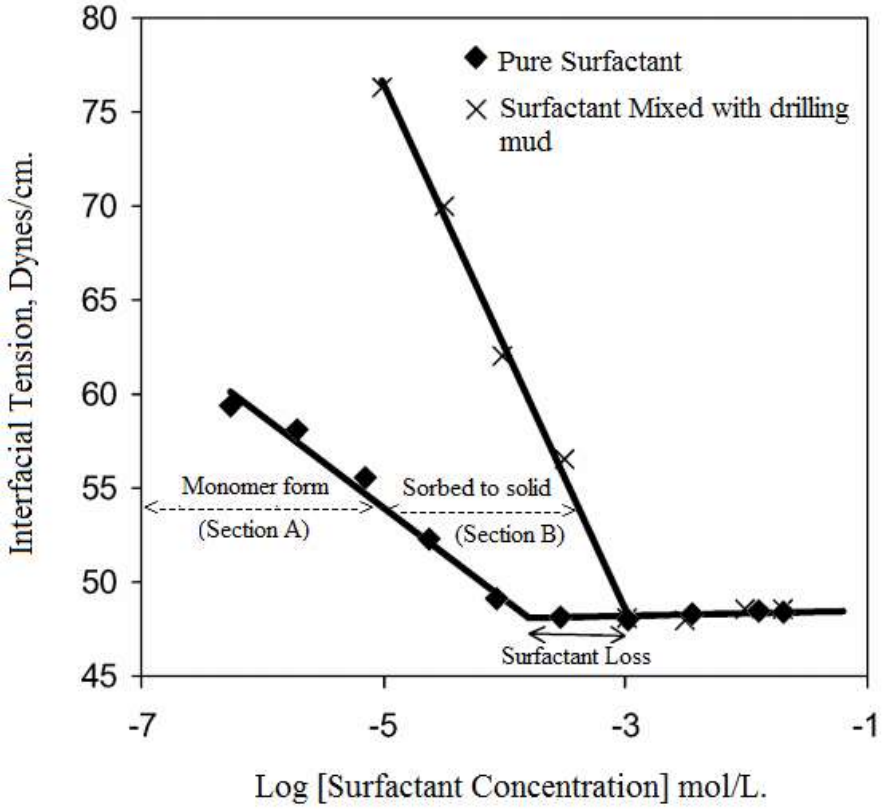


Fig. 4.6 – Surfactant loss measurement by interfacial tension (after Chu and Chan, 2003; Chu and So, 2001)

In the sorption analysis, the approach was similar to the work of Chu and Chan (2003). The experiments were initiated by mixing surfactant solutions at varying concentrations with mud sample at a ratio of 1:6 (vol:mass) to achieve the optimum washing conditions. $HgCl_2$ was added to the solutions to avoid the growth of any bacteria or microorganisms on the solid particles during the analysis (Chu and Chan, 2003; Liu et al., 1991) and to ensure that all surfactant loss is due to sorption to solid particles. The solutions were then stirred for 40 minutes. Finally, the supernatants were separated after centrifuging the

solutions at 3000 rpm for 1 hour, and were sent to IFT measurements with the base oil of synthetic drilling fluid. The complete procedure followed for sorption analysis is illustrated in Figure 4.7.

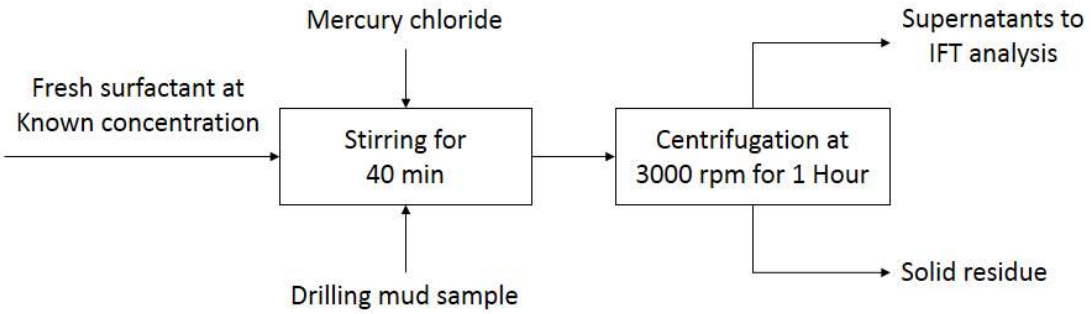


Fig. 4.7 – Procedure employed for surfactant sorption on waste drilling mud by IFT measurements with the base oil of synthetic drilling fluid

4.3.4 Laboratory surfactant-enhanced washing experiments

After selection of the most suitable surfactant, i.e. Triton 100, for the surfactant-enhanced washing of waste drilling mud, based on interfacial and sorption analyses, the effect of three significant factors on the surfactant-enhanced washing efficiencies were investigated. Deionized water was used to dilute the surfactant solutions for washing purposes. The three significant factors were determined to be (i) contact time, (ii) surfactant concentration, and (iii) temperature. The low and high limits of these factors, determined from similar research on soil remediation, are listed in Table 4.2. Surfactant concentration

range was considered to be below CMC to minimize the impact of soil sorption on our experiments. Experiments were conducted using a mechanical shaker at 100 rpm to determine the effects of each parameter and to investigate how changing parameters can affect the petroleum hydrocarbon removal efficiencies of the surfactant-enhanced washing process. Since these three parameters have no or little co-interactions, the effects of the three parameters were experimentally investigated by changing each factor at a time at three levels while keeping other parameters constant at their central values i.e. contact time of 75 minutes, temperature of 30°C, and surfactant concentration of 0.07 wt.%.

Table 4.2 – Parameters influencing petroleum hydrocarbon removal efficiencies for the surfactant-enhanced washing process

Factor	**Unit**	**Range**	
		Low level	**High Level**
Contact time	min	30	120
Surfactant concentration	wt.%	0.05	0.09
Temperature	°C	20	40

After the surfactant washing of the waste drilling mud, the solid particles were separated from the surfactant solution by centrifuging at 1000 rpm for 20 minutes. The aqueous solution was discarded and the remaining solid was analysed for its petroleum hydrocarbon concentrations using the Tier 1 method described in Chapter 3.

Washing tests were completed using a MAXQ 4450 mechanical shaker, manufactured by Thermo Scientific.

4.4 Results and discussions

4.4.1 Interfacial tension analysis

The results of the interfacial tension analysis (between surfactant aqueous solutions and the base oil of synthetic drilling fluid) are plotted in Figure 4.8. The interfacial tension is concentration-dependant and typically decreases with increasing surfactant concentration. The slope of the changing interfacial tension value is higher at the lower concentrations and it moves toward a constant slope (ideally) at higher concentrations and the value of interfacial tension remains constant afterwards (ideally). Lower interfacial tension indicates the oil and surfactant solution are closer to miscibility. When the interfacial tension between the aqueous and hydrophobic compounds is reduced, the forces holding the hydrophobic compounds to the solid particles are also equally reduced (Urum et al., 2005). This reduction causes elevation in both the contact angle and the mobilization of the hydrophobic compounds on the solid surface (Urum et al., 2005). Therefore, Triton 100 is the most effective surfactant for reducing the interfacial tension between the oil and the surfactant solution while Saponin is the least effective surfactant. The lowest interfacial tension achieved by Triton 100 at the concentration of 5% wt.% was 0.285 (±0.005) mN/m. The difference between the three surfactants' interfacial tension was at its highest at the surfactant concentration of 0.25% (wt./wt.%). In practice, employing solutions with lower

surfactant concentrations is desirable for economic reasons and as the Triton 100 has the capability of reducing the interfacial tension at lower concentrations, it can be considered the most suitable surfactant.

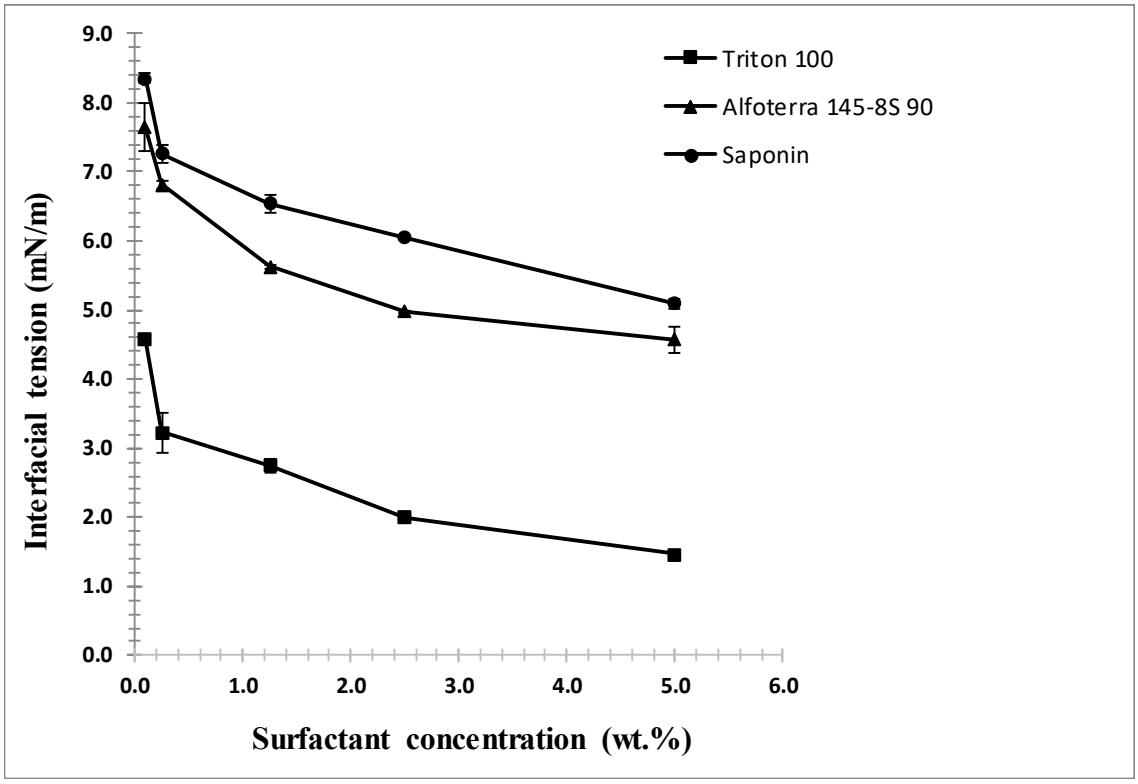


Fig. 4.8 – Interfacial tension of diluted surfactants and synthetic drilling fluid at 22ºC

4.4.1.1 Effect of temperature

Interfacial tension values were measured for the three selected surfactants in two concentrations (0.1 wt.% and 5 wt.%) and the base oil of synthetic drilling fluid at 20°C,

30°C, and 40°C. Figures 4.9, 4.10, and 4.11 show the effect of temperature on the interfacial tension of surfactant aqueous solution and the base oil of synthetic drilling fluid for Triton 100, Alfoterra 145-8S 90, and Saponin respectively. In all cases, the interfacial tension decreases with increasing temperature. Generally, the decrease in the interfacial tension is governed by the reduced viscosities of the hydrophobic compounds in elevated temperatures and their increased mobility causing increases in the contact angles. The differences in the interfacial tension values at different temperatures are less tangible for Triton 100 in the solutions at both low and high surfactant concentrations which can be attributed to the jelly-like nature of Triton 100, possessing high molecular weight and high viscosity (Zubair et al., 2013).

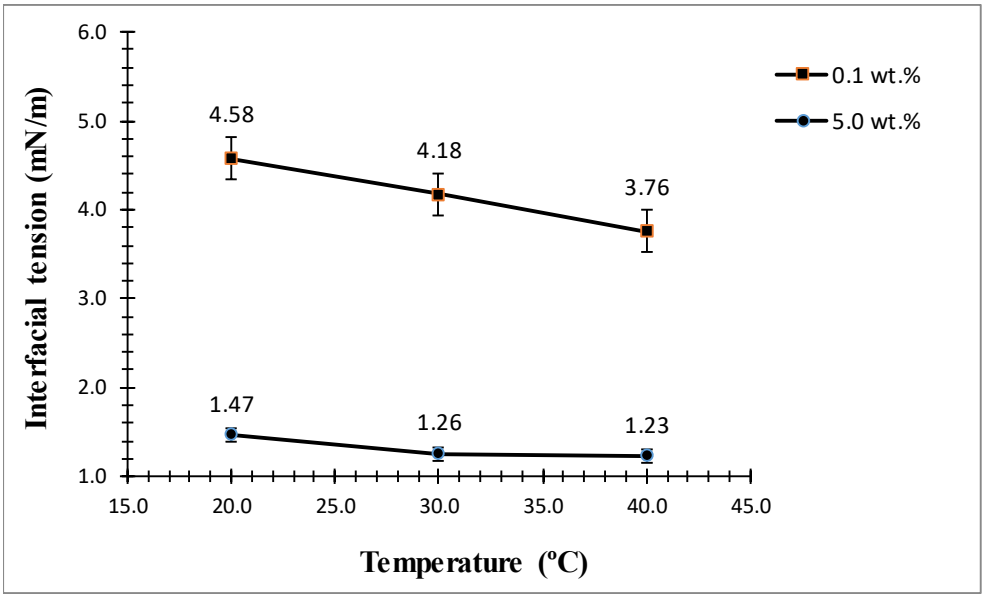


Fig. 4.9 – Effect of temperature on the interfacial tension of Triton 100 aqueous solution and base oil of synthetic drilling fluid at 0.1 and 5.0 wt.% surfactant concentrations

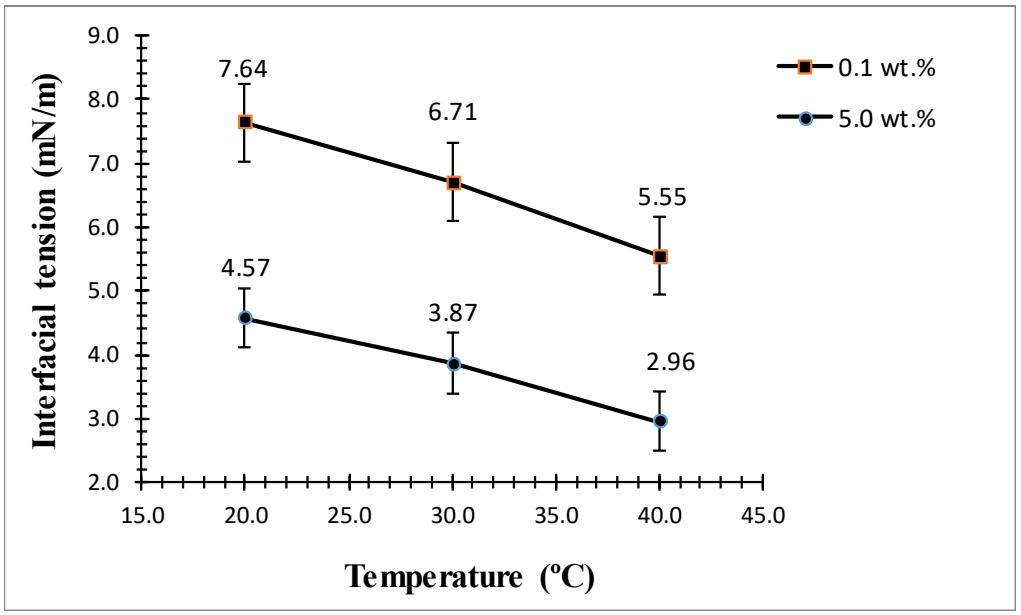


Fig. 4.10 – Effect of temperature on the interfacial tension of Alfoterra 145-8S 90 aqueous solution and base oil of synthetic drilling fluid at 0.1 and 5.0 wt.% surfactant concentrations

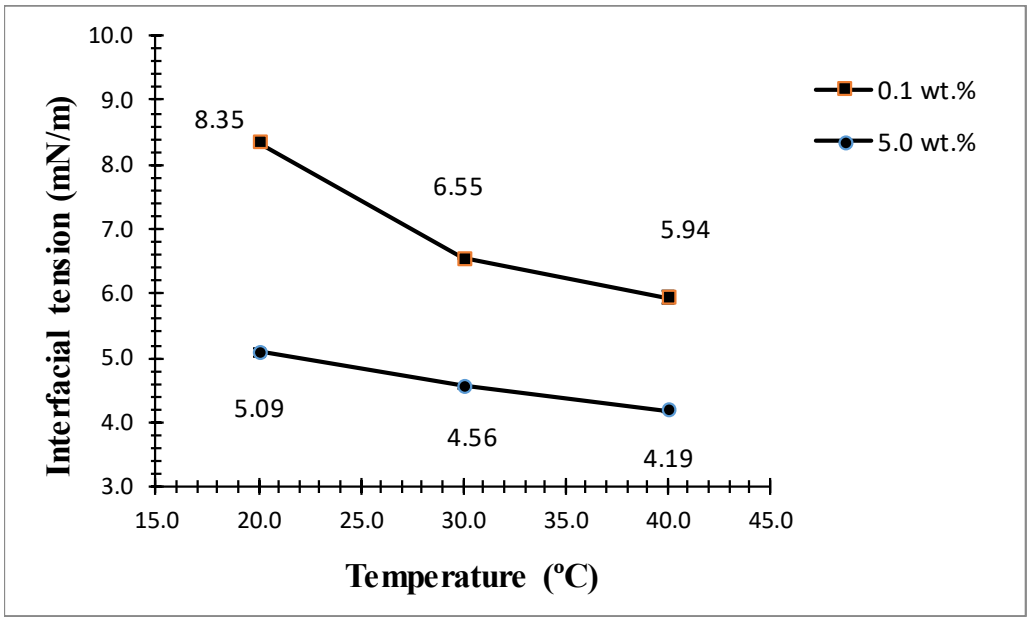


Fig 4.11 – Effect of temperature on the interfacial tension of Saponin aqueous solution and base oil of synthetic drilling fluid at 0.1 and 5.0 wt.% surfactant concentrations

4.4.1.2 Effect of sodium dodecyl sulfate as an additive

Surfactant-enhanced washing with the use of sodium dodecyl sulfate as an additive was previously employed as an effective method for the remediation of petroleum hydrocarbon contaminated soil (Singh and John, 2013). A concentration of 2 wt.% sodium dodecyl sulphate was added to different surfactant solutions at a concentration of 5 wt.%, to evaluate the effect of a modifier in reducing the interfacial tension. The experimental results are listed in Table 4.3. It can be concluded that sodium dodecyl sulphate, in this study for this specific waste remediation process, is not effective in reducing the interfacial tension for Triton 100 and Alfoterra 145-8S 90 surfactants as it is less effective than these two surfactants on its own and weaken their performance; however, its addition can significantly reduce the interfacial tension for the Saponin, the non-ionic biosurfactant. This can be because of the precipitations happening between anionic surfactants and divalent cations such as Ca^{2+} can be reduced when a non-ionic surfactant is also present in the solution. On the other hand, the addition of anionic surfactants may reduce the sorption of non-ionic surfactants, which decreases the surfactant loss (Wei et al., 2015). Despite the reduction in the interfacial tension for Saponin with the addition of sodium dodecyl sulphate as the modifier, the interfacial tension values are still higher than the ones for Triton 100 with or without the addition of the modifier. Therefore, Triton 100 is considered the most suitable surfactant for reducing the interfacial tension.

Table 4.3 – Effect of 2 wt.% sodium dodecyl sulfate on IFT at 5 wt.% surfactant concentration

Surfactant	**Interfacial tension (mN/m)**	
	Without additive	**With additive**
Triton 100	1.47 ±0.03	2.60 ±0.03
Alforterra 145-8S 90	4.57 ±0.09	5.05 ±0.01
Saponin	5.09 ±0.07	4.29 ±0.04

4.4.2 Sorption analysis

The interfacial tension measurements were completed for both the pure surfactant solutions and the supernatants after mixing with the waste drilling mud at various concentrations (with the base oil of synthetic drilling fluid). The inflection points were measured for both systems and the difference between the inflection points' concentrations showed the amount of surfactant loss. The results of the sorption analysis are listed in Table 4.4.

Table 4.4 – Surfactant loss due to sorption to drilling mud for different surfactants

Surfactant	**Inflection point concentration (mN/m)**		**Surfactant loss (%)**
	Pure surfactant	**Supernatants**	
Triton 100	1.316	1.504	12.50%
Saponin	1.182	1.654	28.54%
Alfoterra 145-8S 90	1.317	1.363	3.37%

It can be observed that Triton 100 had an intermediate sorption to the mud solid particles while Saponin loss is higher than both Triton 100 and Alforterra 145-8S 90. Generally, the sorption of the surfactant increases with increasing the surface area and porosity of the solid phase, which may be the reason for high surfactant loss in our experiments. Anionic surfactants were similarly characterized with the least tendency for solid sorption (Park and Bielefeldt, 2003; Kim and Lee, 2000). Since the charge of the solid surface is negative, the least sorption of Alfoterra surfactant can also be attributed to the repulsion between the negative charge of the surfactant's hydrophilic head and the negative charge of the waste drilling mud's surface.

Considering the intermediate sorption and low interfacial tension (with the base oil of synthetic drilling fluid) of our non-ionic surfactant, Triton 100, it was selected as the most suitable surfactant among the three surfactants in the tests for the surfactant-enhanced washing of our waste drilling mud sample.

4.4.3 Surfactant-enhanced washing results

Since the results of the interfacial tension analysis suggested that Triton 100 can be employed as the most suitable surfactant for the surfactant-enhanced washing of the waste drilling mud, the efficiency of the process has been investigated and the effect of temperature, contact time, and surfactant concentration have been determined. The efficiency of the surfactant-enhanced washing process was determined based on the total petroleum hydrocarbon concentration on the remaining solid after washing, as discussed

in section 4.3.3, and its comparison with the initial amounts of petroleum hydrocarbon in the original waste drilling mud sample. Higher concentration of the total petroleum hydrocarbon on the solid shows lower hydrocarbon removal and, thus, less removal efficiency of the surfactant-enhanced washing process.

4.4.3.1 Effect of contact time

The effect of contact time on the removal of petroleum hydrocarbons from the waste drilling mud is illustrated in Figures 4.12 and 4.13. It can be inferred that the maximum petroleum hydrocarbon removal can be achieved in only 30 minutes, after which the concentrations of some petroleum hydrocarbons in the waste drilling mud slightly increase and thus, the petroleum hydrocarbon removal efficiency decreases. Similar observations on the effect of contact time have been reported on surfactant-aided removal of oily contaminants from different solid phases (Chaprao et al., 2015; Lai et al., 2009; Triawan et al., 2017; Urum, 2004). This could be correlated with the surfactant's sorption to the porous structure of the solid particles of the waste drilling mud after a certain amount of time; and therefore, the petroleum hydrocarbon removal decreases as there would be fewer surfactant micelles to remove the oil and petroleum hydrocarbons. This phenomenon can also increase the cost of the process as the surfactant loss may increase after the 30-minute contact time. Thirty minutes should be considered the optimum contact time within the studied range as the maximum efficiency of petroleum hydrocarbon removal up to 70% could be achieved at this stage and the petroleum hydrocarbon removal decreases with increasing the contact time afterwards.

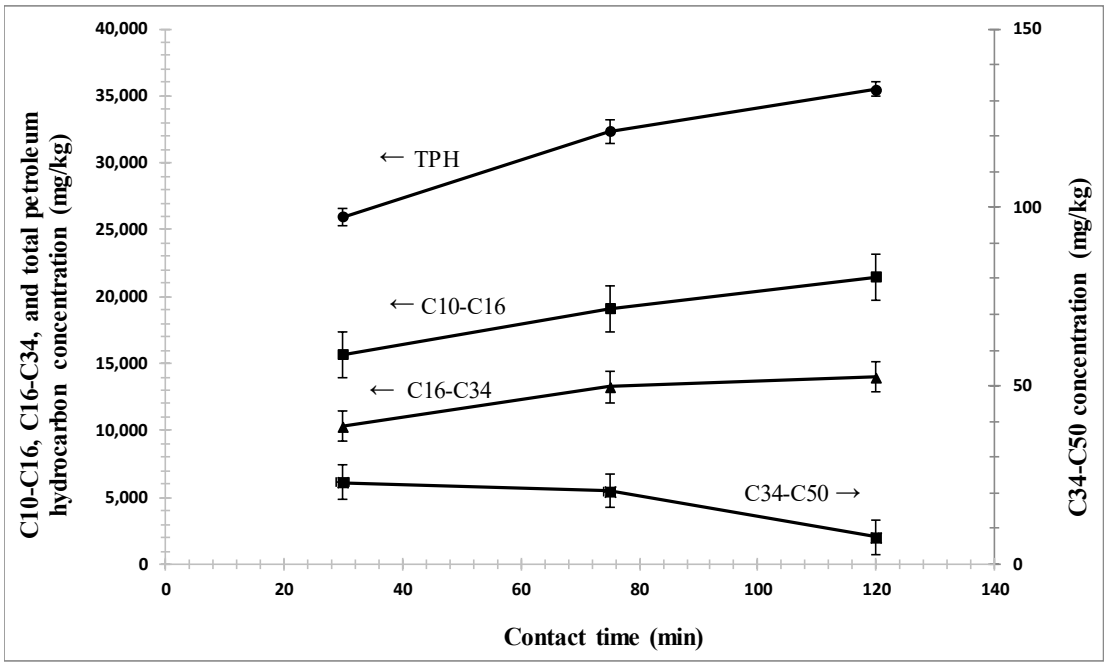


Fig. 4.12 – Effect of contact time on different hydrocarbon fraction concentrations in the waste drilling mud (temperature of 30ºC and Triton 100 concentration of 0.07wt.%)

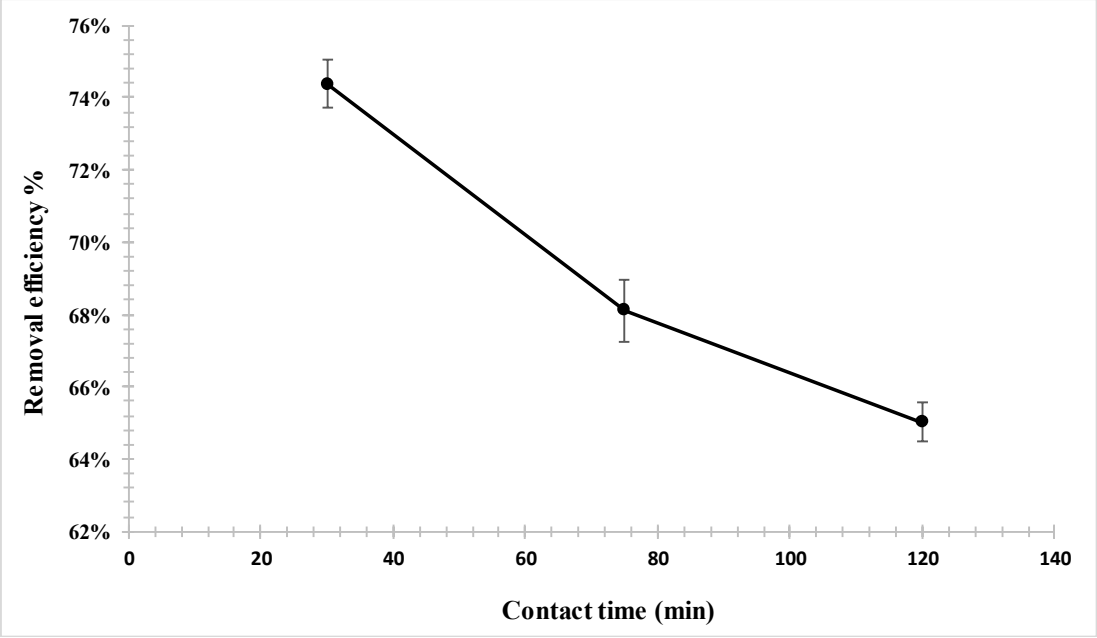


Fig. 4.13 – Effect of contact time on the petroleum hydrocarbon removal efficiency of the surfactant-enhanced washing process (temperature of 30ºC and Triton 100 concentration of 0.07wt.%)

4.4.3.2 Effect of surfactant concentration

The effect of Triton 100 concentration on petroleum hydrocarbon removal are shown in Figures 4.14 and 4.15. Increasing the surfactant concentration improves the hydrocarbon removal efficiencies as the presence of surfactant micelles increases with increasing the surfactant concentration and thus, more oil and petroleum hydrocarbons could be removed and recovered from the waste drilling mud. However, the effect of the surfactant concentration on the removal efficiency is slightly lower in higher concentrations which could be attributed to the fact that the higher concentration provides more surfactant micelles, thus increasing the possibly of surfactant sorption to the waste drilling mud solid particles.

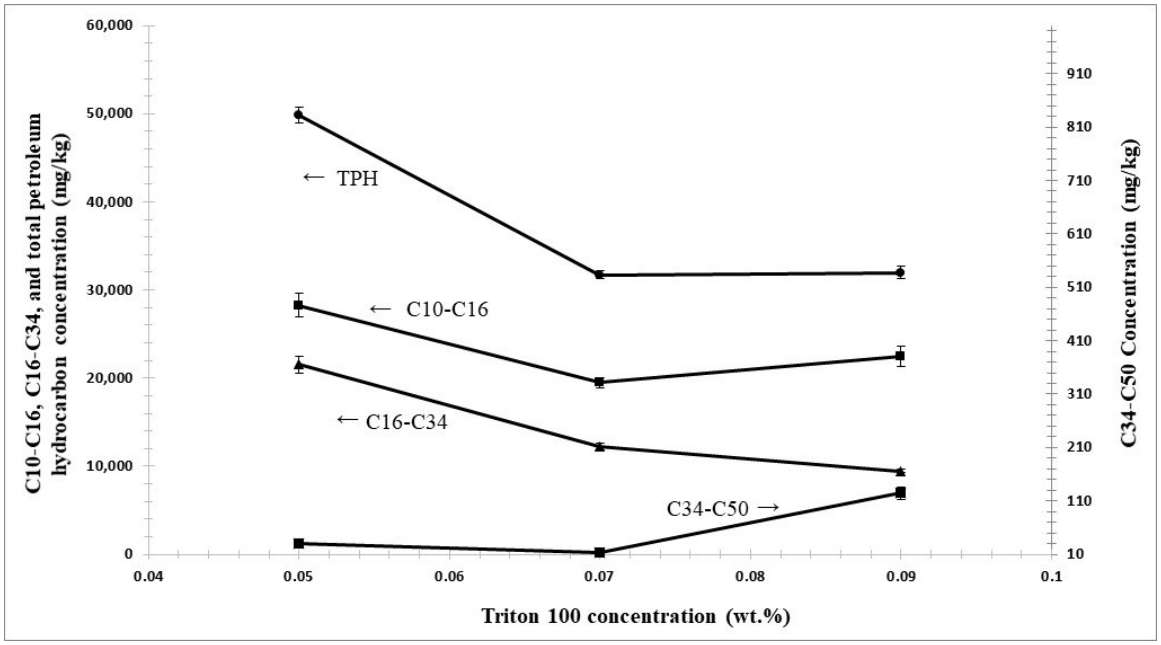


Fig. 4.14 – Effect of Triton 100 concentrations on the removal of various hydrocarbon fractions in the waste drilling mud (temperature of 30ºC and contact time of 75 minutes)

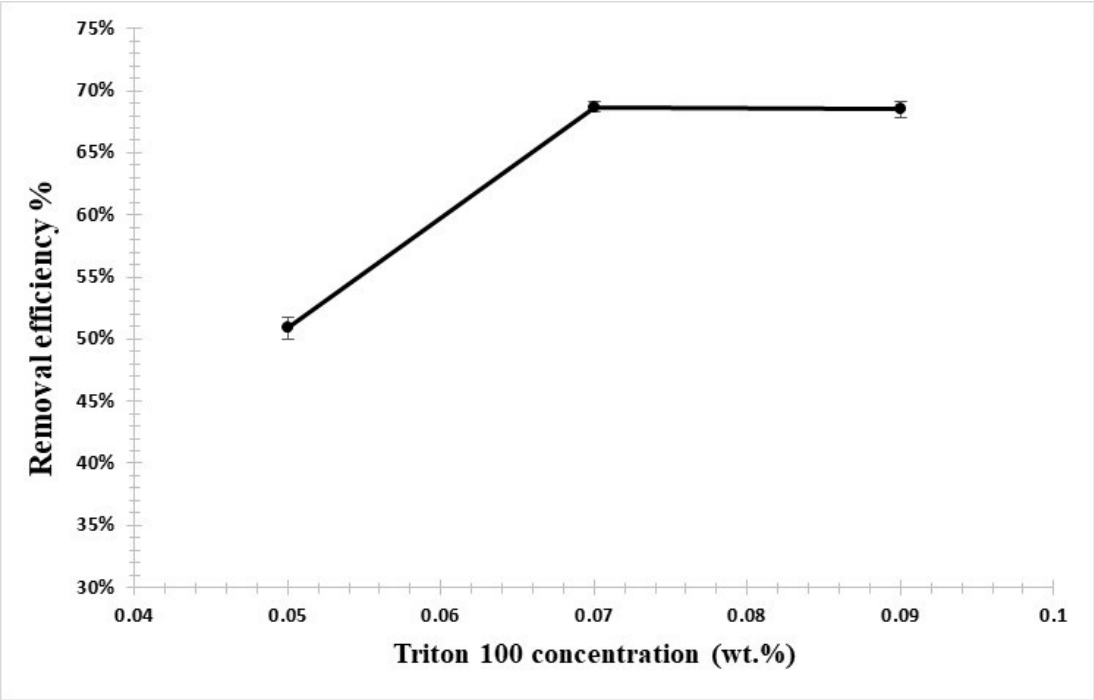


Fig. 4.15 – Effect of Triton 100 concentrations on the petroleum hydrocarbon removal efficiency of the surfactant-enhanced washing process (temperature of 30ºC and contact time of 75 minutes)

4.4.3.3 Effect of temperature

The effects of temperature on the petroleum hydrocarbon concentrations and the removal efficiencies are illustrated in Figures 4.16 and 4.17. There is slight improvement on the petroleum hydrocarbon removal efficiencies by increasing the temperature of the surfactant-enhanced washing process. The temperature increase typically enhances the mobility of the oil molecules due to the reduced viscosity; however, low impact of temperature increase on the petroleum hydrocarbon removal efficiency can be attributed to the jelly-like nature and higher viscosity of the Triton 100 (Zubair et al., 2013).

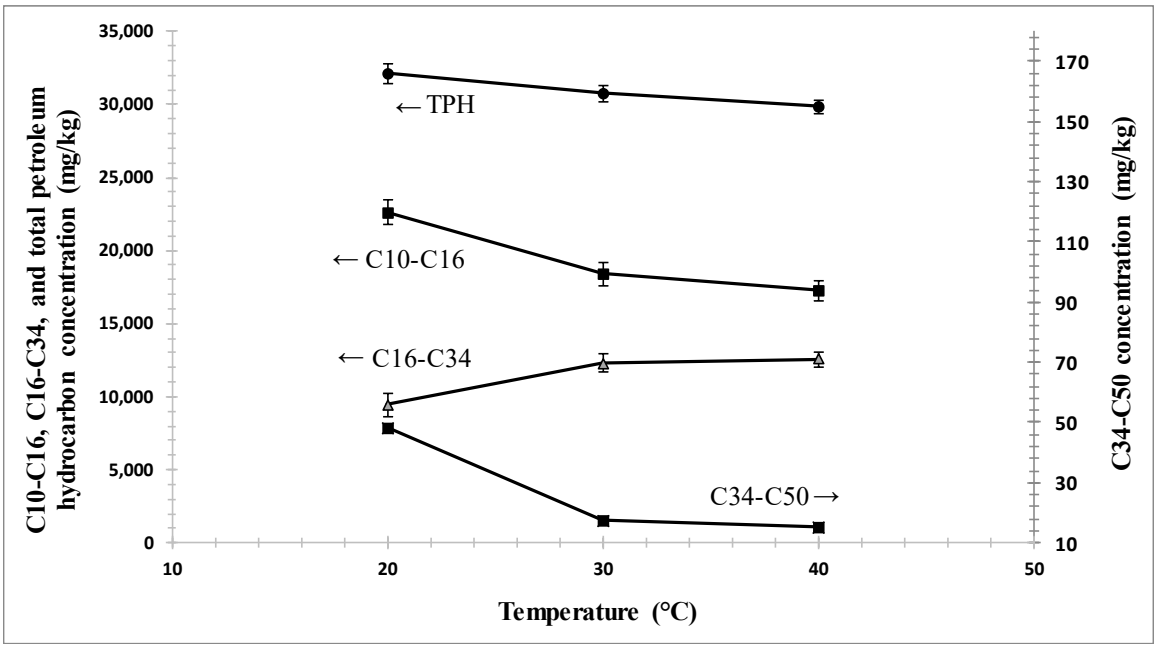


Fig. 4.16 – Effect of temperature on different hydrocarbon fraction concentrations in the waste drilling mud (contact time of 75 minutes and concentration of 0.07 wt.%)

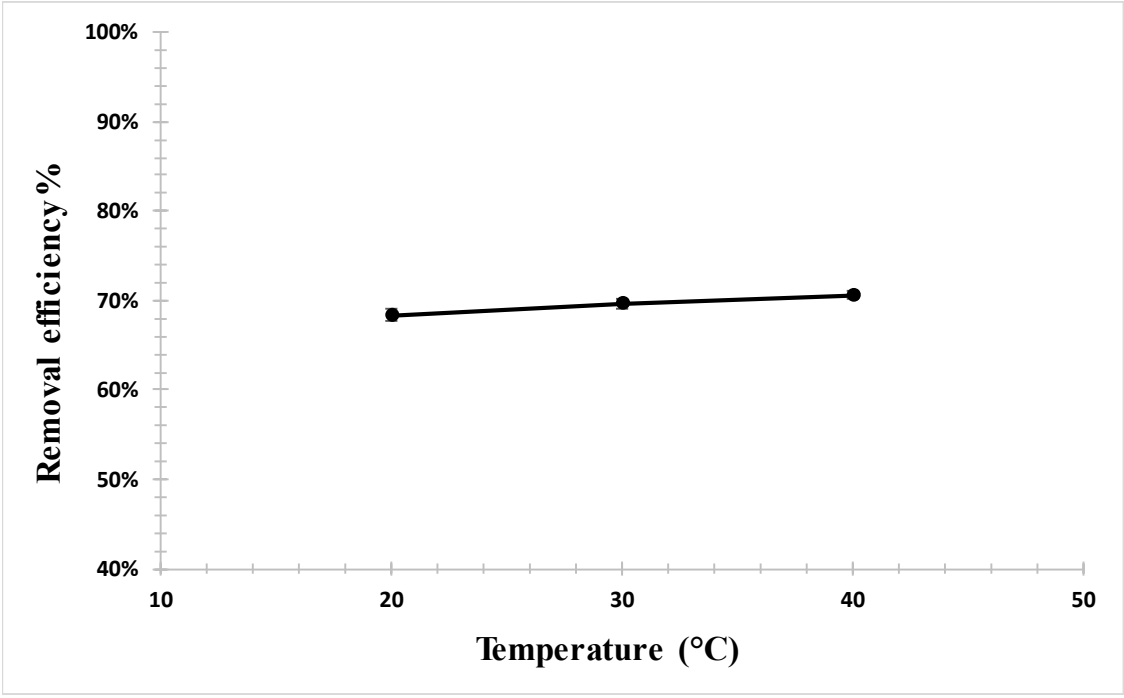


Fig. 4.17 – Effect of temperature on the removal efficiency of petroleum hydrocarbons in the surfactant-enhanced washing process (contact time of 75 minutes and concentration of 0.07 wt.%)

4.5 Summary and conclusions

Three surfactants were experimentally tested for their capability on waste drilling mud surfactant-enhanced remediation. Waste drilling mud was analyzed and surfactants were compared based on their ability to reduce the interfacial tension at different temperatures and with the aid of sodium dodecyl sulfate as an additive. Since the surfactant loss is a significant factor to consider for cost-effectiveness of the washing process, the surfactant sorption to the waste drilling mud solid particles was also measured. After the selection of Triton 100 as the most suitable surfactant for the surfactant-enhanced washing process, it was experimentally tested for the waste drilling mud remediation and the effects of contact time, surfactant concentration, and temperature on petroleum hydrocarbon removal efficiencies were determined. The following are the results obtained from this chapter:

- Triton 100 was selected as the most successful surfactant in reducing the interfacial tension between surfactant aqueous solutions and the base oil of synthetic drilling fluid.
- Interfacial tension between oil and the surfactant solutions were the lowest in case of Triton 100 and the highest in case of Saponin.
- Increasing temperature was generally effective in reducing the oil/water interfacial tension. This is attributed to the reduced viscosity and increased mobility of the hydrophobic phase.
- The addition of anionic sodium dodecyl sulphate was only effective in case of Saponin, as the non-ionic biosurfactant, to reduce the oil/water interfacial tension.

- Loss of the surfactants due to sorption to solid particles was minimal for Alfoterra 145-8S 90 and maximum for Saponin. The least sorption of the Alfoterra surfactant was attributed to the high pH and the negative charge of the solid surface of the waste drilling mud.
- Thirty minutes were considered as the optimum time to achieve the highest total petroleum hydrocarbon removal efficiency using Triton 100 in the surfactant-enhanced washing process
- Increasing temperature slightly improved the efficiency of the surfactant-enhanced washing of the waste drilling mud by Triton 100 due to enhancement of the mobility of the oil molecules and reduced viscosity; however, the impact of temperature was not considered significant. Therefore, a temperature of 20ºC was considered the optimum temperature for our surfactant-enhanced washing process from technical and economic perspectives.
- Increasing Triton 100 concentration could result in higher petroleum hydrocarbon removal efficiencies due to the increase in the available micelles in the solution up to a certain amount at the surfactant concentration of 0.07 wt.% which is considered the optimum surfactant concentration.
- The results suggested that Triton 100 is a good candidate for the remediation of waste drilling mud; however, further treatment may be required to reach the limits of environmental regulations in place for disposal and landfilling of the waste drilling mud.

Chapter 5: Development and Optimization of the Supercritical CO_2 Extraction Process to Treat the Waste Drilling Mud

5.1 Introduction

The application of the supercritical CO_2 extraction process has recently been investigated for the treatment of various oily contaminants such as waste drilling mud and cuttings (Lopez-Gomez, 2004; Odusanya, 2003; Street et al., 2007). Supercritical CO_2 extraction can typically separate the petroleum hydrocarbons easily and without damaging the solid waste (Odusanya, 2003; Street et al., 2007).

The details of the supercritical fluid extraction process and its application on the remediation of waste drilling mud and cuttings were mainly discussed in Chapter 2. Above the critical temperature and pressure, the supercritical substance (in this case CO_2) possesses gas-like diffusivities and viscosities, liquid-like densities, pressure-dependent solvating power, and zero surface tension (Street et al., 2007, McHugh and Krukonis, 2013). Gas-like diffusivities and viscosities help the supercritical CO_2 to pass through the solid particles while the liquid-like densities mean lower amounts of supercritical carbon dioxide, for the same volume compared to gas, can be employed for the treatment process.

CO_2 is the mostly used solvent among other supercritical fluids. Its wide application is due to its inertness, near-ambient critical temperature (T_c = 31 ºC), non-flammability, non-toxicity, universal availability, and its relatively low cost (Saintpere and Morillon-Jeanmaire, 2000). CO_2 also provides high solvating power at pressures a little above its

critical pressure (Saintpere and Morillon-Jeanmaire, 2000). The solvent properties of the carbon dioxide depend on its density and can be altered by the temperature and pressure adjustments (Lopez-Gomez, 2004; Cripps, 1998; Mansoori, 2003). Increasing the pressure of carbon dioxide causes increases in its density and improvement of its extractive power (McHardy and Sawan, 1998). The supercritical carbon dioxide solubility of organic compounds also increases with higher densities (Yamada et al., 2017). Table 5.1 lists the complete range of density values for different temperatures and pressures (McHardy and Sawan, 1998).

Table 5.1 – Density of carbon dioxide (CO_2) at different temperatures and pressures

(McHardy and Sawan, 1998)

Temp °C	Pressure (atm)											Density (g/ml)
	150	200	250	300	350	400	450	500	550	600	650	
20	0.9062	0.9392	0.9652	0.9869	1.005	1.022	1.037	1.051	1.063	1.075	1.086	
30	0.8496	0.8930	0.9249	0.9505	0.9721	0.9909	1.007	1.022	1.036	1.049	1.061	
40	0.7832	0.8427	0.8823	0.9127	0.9376	0.9588	0.9775	0.9941	1.009	1.023	1.035	
50	0.7033	0.7875	0.8373	0.8734	0.9022	0.9262	0.9470	0.9654	0.9818	0.9969	1.010	
60	0.6098	0.7274	0.7899	0.8329	0.8660	0.8932	0.9163	0.9365	0.9545	0.9707	0.9855	
70	0.5155	0.6639	0.7408	0.7914	0.8294	0.8598	0.8854	0.9075	0.9271	0.9446	0.9605	
80	0.4376	0.6004	0.6909	0.7495	0.7924	0.8264	0.8546	0.8787	0.8998	0.9187	0.9357	
90	0.3804	0.5410	0.6417	0.7077	0.7556	0.7931	0.8239	0.8500	0.8728	0.8930	0.9112	
100	0.3392	0.4888	0.5949	0.6669	0.7194	0.7603	0.7936	0.8217	0.8461	0.8676	0.8869	
110	0.3086	0.4448	0.5517	0.6279	0.6843	0.7282	0.7639	0.7940	0.8199	0.8427	0.8631	
120	0.2849	0.4083	0.5128	0.5913	0.6506	0.6971	0.7350	0.7668	0.7942	0.8183	0.8397	
130	0.2660	0.3782	0.4784	0.5575	0.6187	0.6673	0.7071	0.7405	0.7692	0.7944	0.8169	
140	0.2503	0.3532	0.4482	0.5265	0.5889	0.6390	0.6803	0.7151	0.7450	0.7713	0.7946	
150	0.2371	0.3321	0.4218	0.4985	0.5611	0.6122	0.6547	0.6907	0.7217	0.7489	0.7730	

Figure 5.1 shows the density of supercritical carbon dioxide as a function of temperature with parametrically changing pressure (Ely, 1986). Decreasing the pressure or increasing the temperature can result in lower densities of the supercritical carbon dioxide that may be disadvantageous in the removal and recovery of organic compounds.

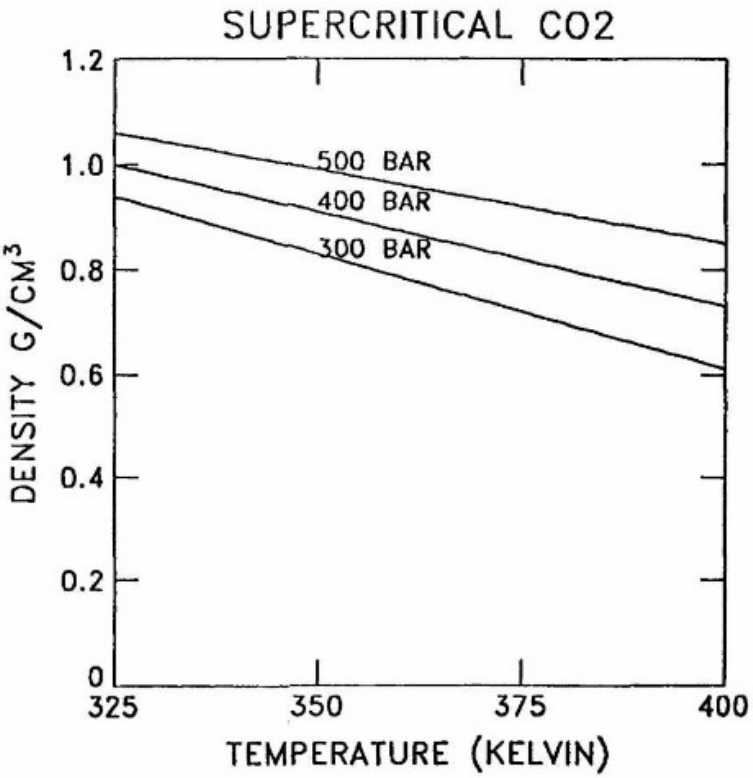


Fig. 5.1 - Effect of temperature and pressure on the density of supercritical CO_2 (Ely, 1986)

In Figure 5.2, the viscosity of the supercritical carbon dioxide is plotted against changing temperature and pressure, showing how increasing pressure or decreasing temperature can

result in increased viscosity. Therefore, increasing temperature or reducing pressure reduce both viscosity and density. Lowering viscosity of the solvent (in this case CO_2) is favorable for solubilisation of organic compounds from contaminated solids due to increased mass transfer (McHardy and Sawan, 1998). However, lower density reduces the supercritical carbon dioxide extractive power.

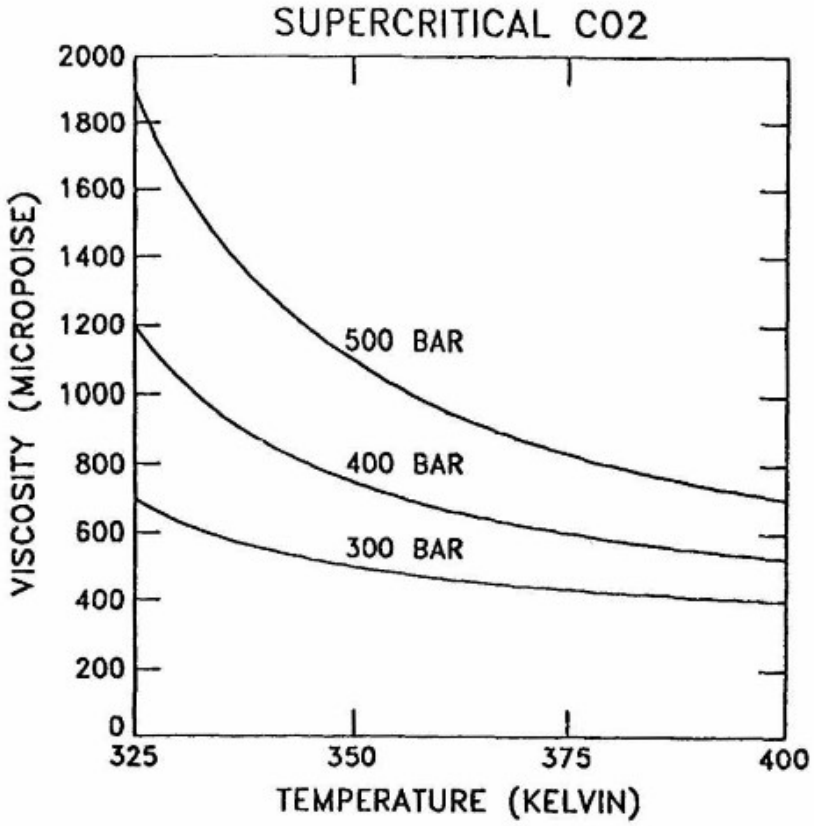


Fig. 5.2 - Effect of temperature and pressure on the viscosity of supercritical CO_2 (Reid et al., 1977)

In this chapter, the procedure followed for the removal and recovery of petroleum hydrocarbons from the waste drilling mud by the supercritical CO_2 is discussed in detail. Significant factors affecting the supercritical extraction process and their effects are determined, and the operating conditions are optimized using the Box-Behnken design (BBD). Box-Behnken design is a technique from the response surface methodology (RSM), considered an interesting and challenging tool to optimize different processes (Cornell, 1990).

Box-Behnken design is ideal for three varying parameters resulting in the minimum number of designed experiments. Box-Behnken design is one of the second-order designs of the response surface methodology based on three-level incomplete factorial designs (Ferreira et al., 2007). Previous studies have compared the Box-Behnken design with central composite design (CCD) and the three-level full factorial design. Results showed that Box-Behnken design is considered a marginally more efficient method than the central composite design and a considerably more effective technique than the three-level full factorial design (Ferreira et al., 2007). The Box-Behnken design is also sufficient to assign a typical quadratic model to the experimental results. Therefore, in the current study, the Box-Behnken design was selected to design experiments and optimize the supercritical CO_2 extraction process.

The results of the removal and recovery efficiencies of different petroleum hydrocarbon fractions and the total concentrations are presented. A polynomial model based on the experimental results is also presented to predict the supercritical CO_2 extraction process based on the changes of significant parameters.

5.2 Materials and methods

Supercritical CO_2 extraction experiments were conducted to investigate the ability of the process to reduce the concentration of total petroleum hydrocarbons of the waste drilling mud. In this section, materials and equipment employed for the process are listed and the details on designed experiments, analysis of variance (ANOVA), and process optimization are provided which ensure the reproducibility of the results.

5.2.1 Chemicals and equipment

The waste drilling mud was provided by Environmental Universal Ltd. and the supercritical fluid employed in this study was the Carbon Dioxide (CO_2), supercritical fluid chromatography (SFC) grade, with 2000 psi Helium Pad (4.8 – 99.99%), supplied by Praxair Canada Inc.

A Teledyne Isco D-series syringe pump (model 260D, Teledyne Isco Inc.) attached to a cooling jacket and equipped with a reservoir to cool, store, and deliver the liquid carbon dioxide was used in the supercritical experimental setup. The extraction vessel used in the setup was supplied by Penn Manufacturing Inc. (ID - 1.974×10^{-2} m, height – 4.46×10^{-2} m, 10000 Psig @194 ºF) and the heating tape was provided by Omega Engineering Inc. (model: HTWC101-010). The flowmeter used at the end of the experimental setup was provided by Aalborg Instruments & Controls Inc. (XFM Series). All the other chemicals and materials were at the same grade as employed in previous sample analyses.

5.2.2. Design of experiments (Box-Behnken design)

For the supercritical extraction process, the Box-Behnken design of the response surface methodology technique was employed to design the minimum number of experiments required to investigate the effect of three parameters on the removal and recovery of petroleum hydrocarbons from the waste drilling mud, to develop a polynomial model based on the experimental results, and to optimize the supercritical CO_2 extraction process.

Three parameters were considered as the most significant factors affecting the process' efficiency: (i) temperature, (ii) pressure, and (iii) contact time, designated as A, B, and C respectively. These factors and their limit values were considered as a result of the literature review on research conducted on different supercritical CO_2 extraction processes. Table 5.2 lists the minimum and maximum levels for each parameter. Table 5.3 lists the designed experiments using these parameter levels. Experiments were conducted based on the design matrix of the Box-Behnken design with five centre points replicates. These five-center point replicates are the recommended number of center points by the Design Expert® software which should not be reduced as the center levels provide better predictions in the respective areas. Furthermore, the replicates provide an accurate lack-of-fit test (Stat ease Inc., 2016). It is recommended by the software that these five center point experimental runs be randomly conducted.

Table 5.2 - Process variables and their limit values for the supercritical CO_2 extraction process

Factor	**Low**	**High**
A: Temperature (ºC)	40	60
B: Pressure (MPa)	10	20
C: Contact time (min)	30	120

Table 5.3 - Design of experiments using Box-Behnken design

Run	**A Temperature (ºC)**	**B Pressure (MPa)**	**C Contact time (min)**
1	60	15	30
2	60	15	120
3	50	10	30
4*	50	15	75
5	60	10	75
6*	50	15	75
7*	50	15	75
8*	50	15	75
9	50	10	120
10	40	10	75
11	60	20	75
12	40	20	75
13	50	20	30
14	50	20	120

15	40	15	30
16	40	15	120
17*	50	15	75

Five marked points (4, 6, 7, 8, 17) are center point replicates recommended by the software to ensure the repeatability, predictions, and accurate lack-of-fit test results.

All seventeen experiments were performed in random sequences to avoid or minimize the effects of uncontrolled factors. The replicate points are the verification tool that can specifically help the software to measure the accuracy of the predicted models and their pure errors. When the results of the replicates are not similar, they affect the accuracy of the models. These accuracies can be observed in the ANOVA results (Appendix V).

5.2.3 Prediction of petroleum hydrocarbon removal and recovery using Design Expert®

Design Expert® software was employed to develop a polynomial model to predict the petroleum hydrocarbon removal and recovery efficiency by the supercritical CO_2 extraction process. The fitted model is a suitable resource to accurately predict the efficiency of hydrocarbon removal and recovery using parameter levels outside of the considered limits, and to determine the scale of importance for each parameter on the efficiency of the supercritical CO_2 extraction process. A larger coefficient in the model represents a more significant effect of the respective parameter. The polynomial model's plus or minus signs for different coefficients represent negative or positive impacts of the

respective parameters on the process' efficiency. The predicted model and its details are included in Appendix V.

5.2.4 Analysis of variance (ANOVA)

A least-squares fit procedure was applied to estimate the coefficients of the polynomial model for the petroleum hydrocarbon removal and recovery efficiency. The generated model developed by the Design Expert® software and its statistical importance were evaluated by the Fisher test (F-test). F-test is typically calculated by dividing the model mean square by its residual mean square for the analysis of variance (ANOVA). Analysis of variance evaluates the significance of the predicted model by Design Expert®. The detailed ANOVA results are listed in Appendix V.

5.2.5 Optimization

Optimum conditions for the removal and recovery of petroleum hydrocarbons using the supercritical CO_2 extraction were determined using the optimization tool of the Design Expert® software. The objective of the programme is to optimize multiple responses so that a "desirability function" between 0 and 1 can be maximized. The desirability function as defined by the Design Expert® software is "*simply a mathematical method to find the optimum conditions. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. The value is completely dependent on how closely the lower and upper limits are set relative to the actual optimum. The goal of optimization is to find*

a good set of conditions that will meet all the goals, not to get to a desirability value of 1.0" (Stat ease Inc., 2016). The concentrations for all hydrocarbon fractions and thus the total petroleum hydrocarbons were targeted to be at their minimum levels and their removal and recovery were targeted to be at the maximum levels. All parameters were also defined to be in the design range.

5.2.6 Supercritical CO_2 extraction procedure

The supercritical CO_2 extraction experimental setup used in this study is illustrated in Figure 5.3. When the CO_2 reaches the intended pressure and temperature, it gets mixed with the waste drilling mud in the extraction vessel for a specified amount of time. Heating tape was employed to cover all the CO_2 lines to ensure constant temperature was maintained for each experiment. The CO_2 gets separated at the end of the process by sudden pressure drop and the oil was recovered in the collector.

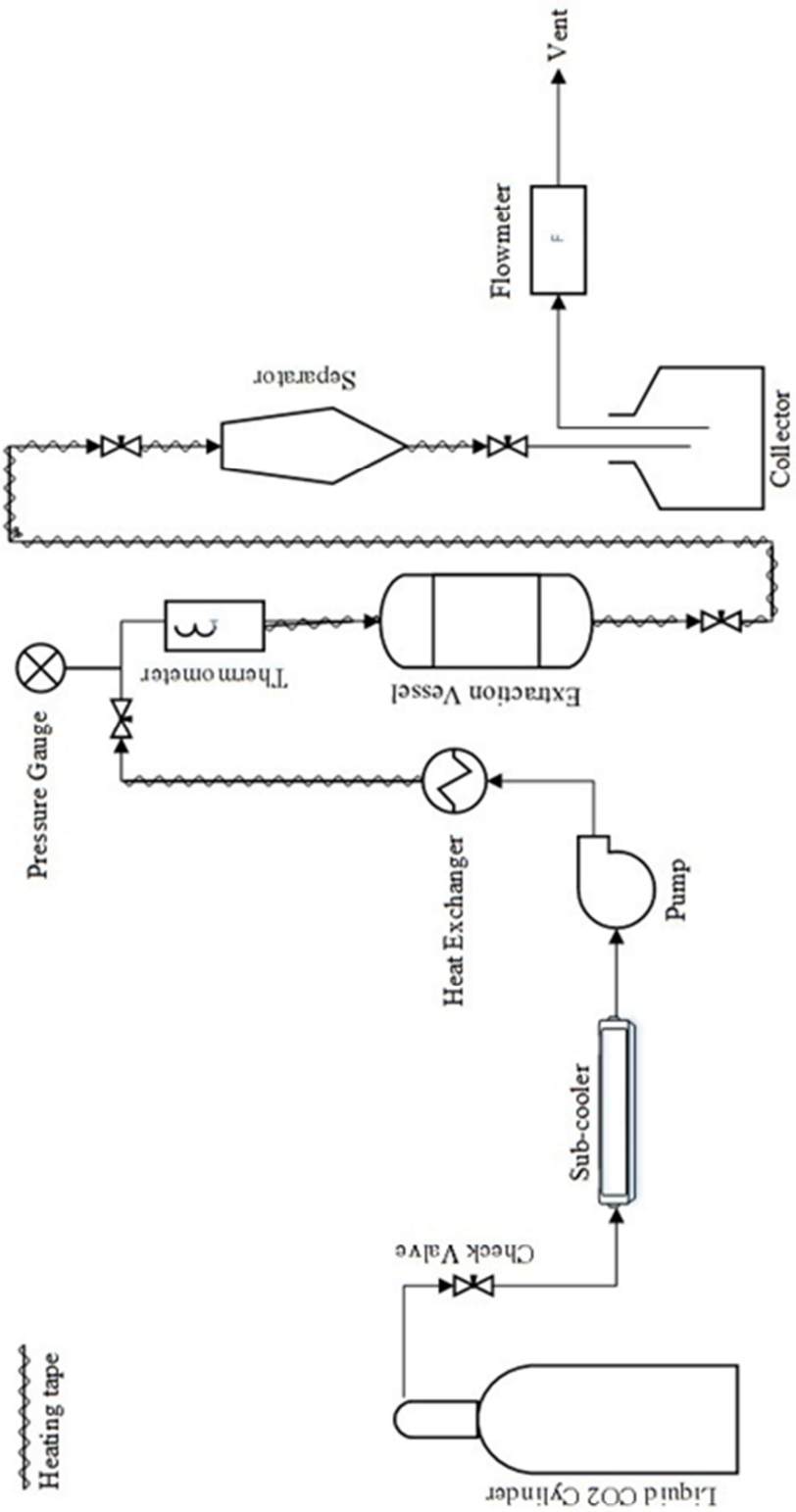


Fig. 5.3 - Schematic diagram of the supercritical CO_2 experimental setup

To start the experimental procedure, 10-12g of the waste drilling mud sample were weighed and placed in the extraction vessel connected to the delivery tubes, all of which were covered by the heating tapes to keep the specified temperature constant and steady for the entire system. The pressure (ranging from 10 to 20 MPa) and temperature (ranging from 40 to 60 ºC) for each experiment were set based on the experimental design matrix (Box-Behnken design). When the liquid CO_2 was taken from a pressurized cylinder and was compressed to the specified pressure, the experiment started by pumping the supercritical gas to the extraction vessel and the flow rate was kept constant at 2 ml/min by adjusting the checking valve prior to the separator. The process was continuously conducted for a specific amount of time based on the experimental design matrix (between 30 to 120 minutes). At the end of the process, the gas was depressurized in the collector and thus, the petroleum hydrocarbons were separated/deposited into the collector. The separated oil sample and the solid residue sample were collected and weighed, and the solid residue was submitted for the hydrocarbon determination analysis. Figure 5.4 shows the waste drilling mud sample before and after the supercritical CO_2 extraction, and the recovered oil in the collector.

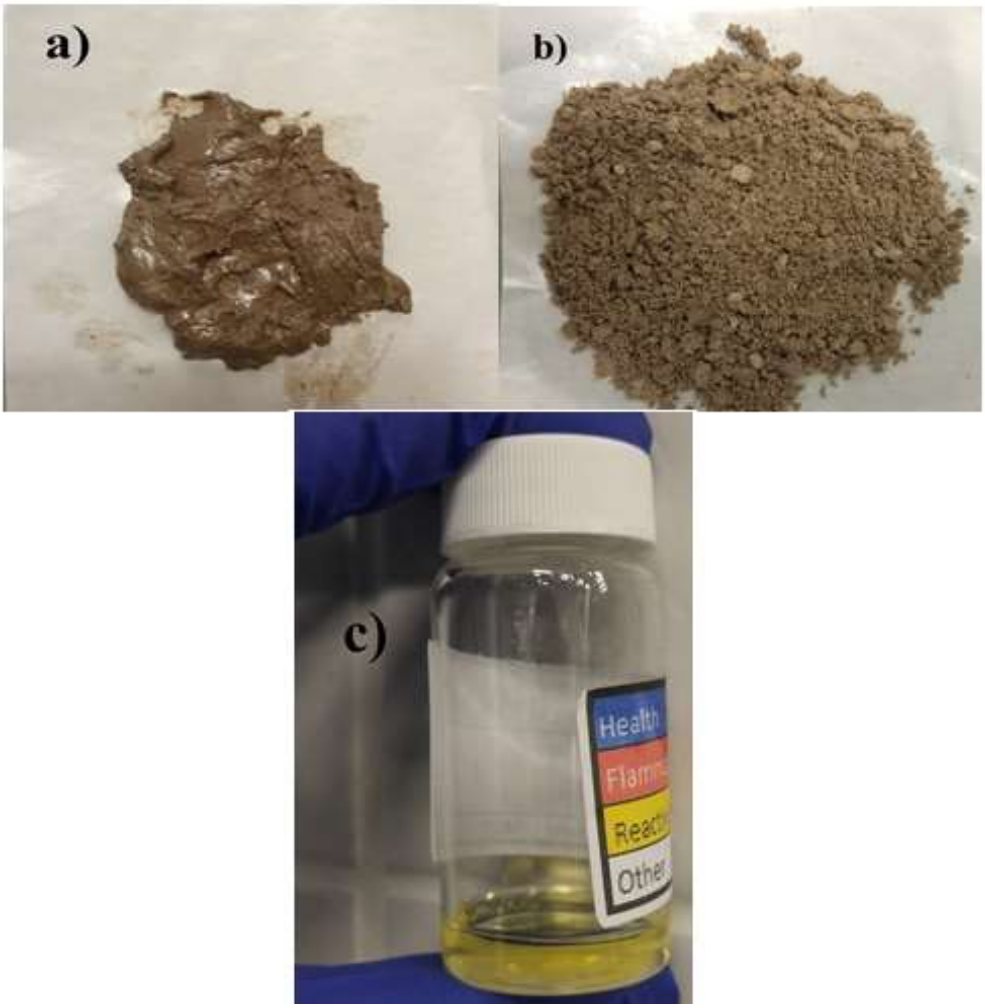


Fig. 5.4 – a) Waste drilling mud before any treatment, b) solid residue after the waste drilling mud treatment by supercritical CO_2 extraction, and c) recovered oil in the collector (operating conditions: temperature: 50 ºC, pressure: 15 MPa, and contact time: 75 minutes)

5.2.7 Hydrocarbon removal and recovery efficiency analysis

The waste solid residue after the supercritical CO_2 extraction was analyzed and compared to the initial waste drilling mud to determine the efficiencies of the process on different concentrations of hydrocarbon fractions and total petroleum hydrocarbons. The Tier 1 method (CCME, 2007) was employed to determine the petroleum hydrocarbon concentrations (after the supercritical CO_2 extraction process) and the removal and recovery efficiencies, as described in Chapter 3.

5.3 Results and discussion

The experimental results of the hydrocarbon fraction concentrations and the removal and recovery efficiency of the petroleum hydrocarbons are listed in Appendix IV. The results showed that more than 97% of the petroleum hydrocarbons could be removed and recovered using the supercritical CO_2 extraction process. The surface plots (3D) of the effect of temperature, pressure, and contact time are illustrated in Figure 5.5. The effect of contact time is more significant than the effect of pressure while the effect of temperature is the least significant on the removal and recovery efficiency of total petroleum hydrocarbon from the waste drilling mud.

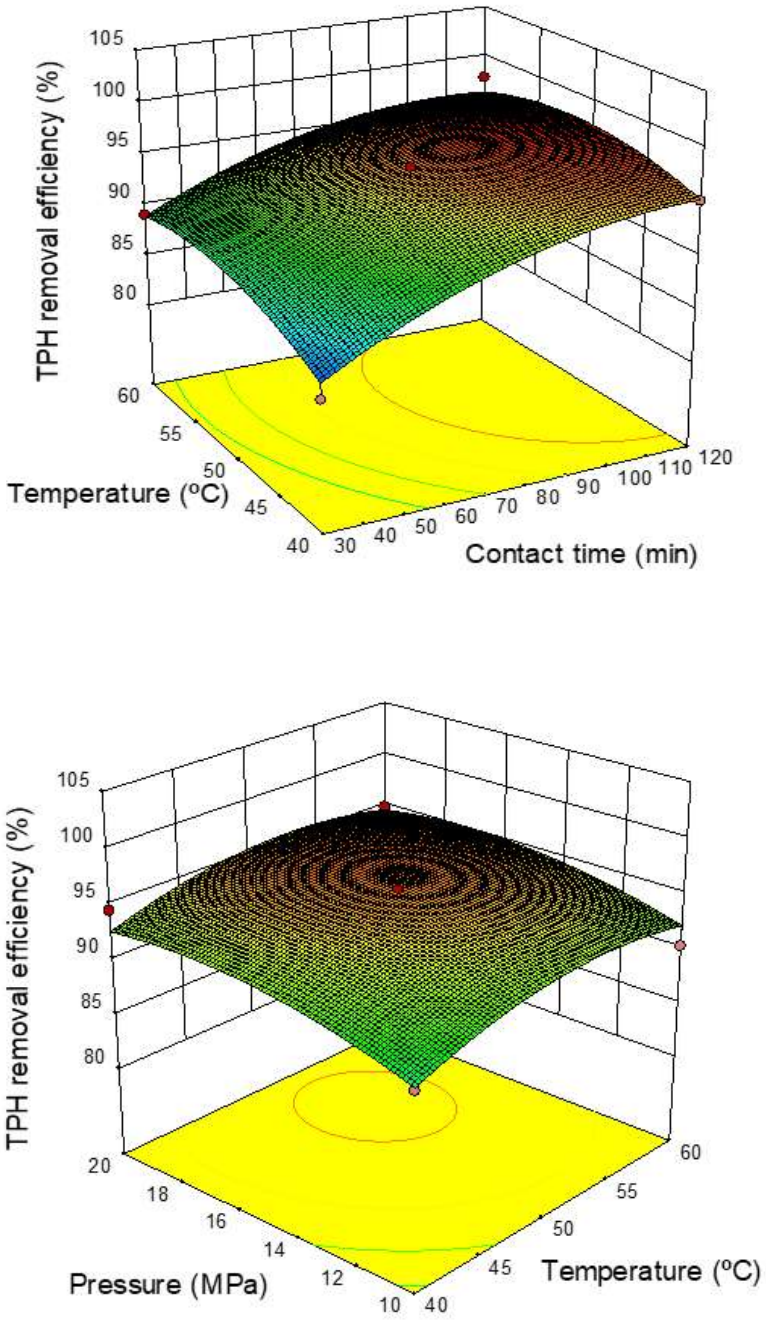


Fig 5.5 – The surface plots illustrating the effects of (top) temperature and contact time at a pressure of 15 MPa and (bottom) pressure and temperature at a contact time of 75 minutes on the total petroleum hydrocarbon removal efficiencies

The effect of three significant parameters, including temperature, pressure, and contact time, performance prediction of the supercritical CO_2 extraction process to remove and recover petroleum hydrocarbons, and process optimization are discussed below all of which are results of experimental investigation. The confidence intervals (CI) of 95% are shown in all figures.

5.3.1 Effect of temperature

The effect of temperature on the removal and recovery of different hydrocarbon fractions and the total petroleum hydrocarbons is illustrated in Figure 5.6. Increasing temperature decreases the concentration of C16-C34 and C34-C50 hydrocarbon fractions. However, for C10-C16 the concentrations of petroleum hydrocarbons were reduced to 3,547-3,866 mg/kg and then slightly increased. This indicates there is an optimum temperature where the removal and recovery efficiency can be maximized.

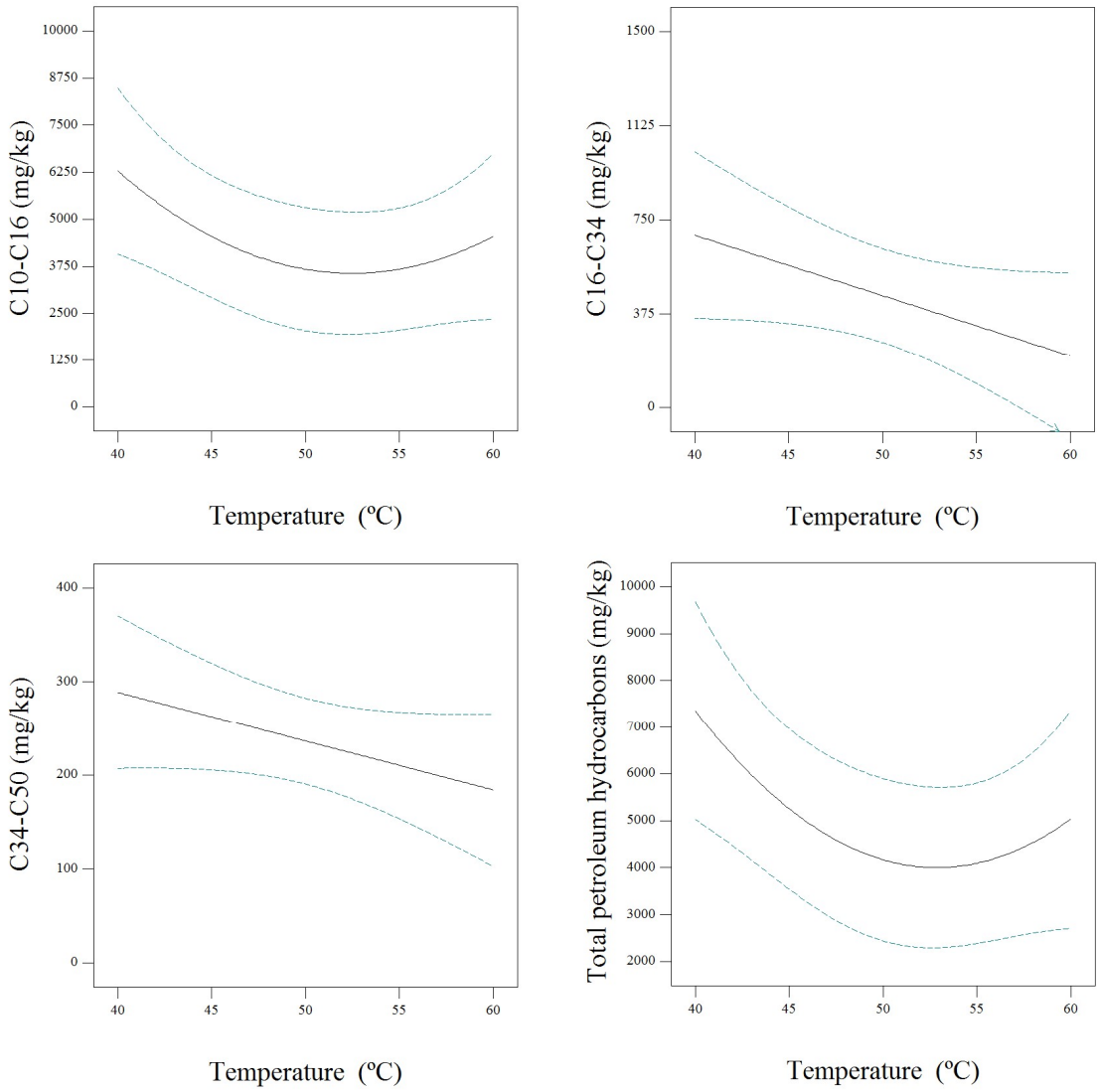


Fig. 5.6 – Effect of temperature on the removal and recovery of petroleum hydrocarbons at a contact time of 75 minutes and a pressure of 15 MPa (Initial concentrations of C10-C16 hydrocarbons: 65,298 mg/kg; C16-C34 hydrocarbons: 34,320 mg/kg; C34-C50 hydrocarbons: 1,800 mg/kg; and total petroleum hydrocarbons: 101,418 mg/kg)

The effect of temperature on the removal and recovery efficiency of petroleum hydrocarbons for the supercritical CO_2 extraction process is illustrated in Figure 5.7. Increasing the temperature results in increasing the efficiency to more than 95% and then the efficiency slightly decreases. A quadratic model was suggested by the Design Expert® software for the process efficiency with an R-Squared of 0.93. An optimized temperature needed to be determined in the range to ensure the maximum efficiency could be reached.

The increase in the efficiency of hydrocarbon removal and recovery by increasing the temperature can be attributed to the fact that elevated temperatures typically increase both the mobility of the petroleum hydrocarbons and the contact angle between the oil and the solid surface of the waste drilling mud (due to the reduced viscosity of organic compounds). The volatility of the oil also increases at higher temperatures. The slight decrease observed for the removal and recovery efficiency at the end can be due to the decrease in the CO_2 density at higher temperatures as observed in Figure 5.1 and Table 5.1 (Lopez-Gomez, 2004, McHardy and Sawan, 1998). It has been discussed that higher densities of the supercritical fluid, i.e. liquid-like densities, can assist the extraction process to gain higher efficiencies (Odusanya, 2003, McHardy and Sawan, 1998). Therefore, the effect of the temperature on the removal and recovery efficiency is not linear.

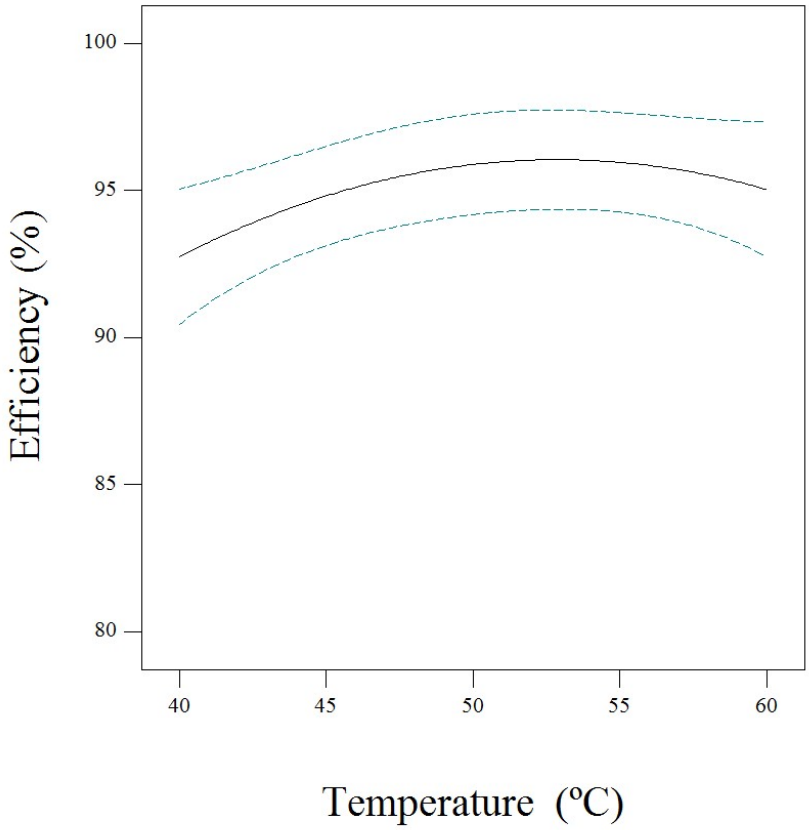


Fig. 5.7 – Effect of temperature on the removal efficiency of total petroleum hydrocarbons for the supercritical CO_2 extraction process (contact time of 75 minutes and pressure of 15 MPa)

5.3.2 Effect of pressure

The effect of pressure on the removal and recovery of petroleum hydrocarbons, illustrated in Figure 5.8, is similar to the effect of temperature on C10-C16 and total hydrocarbons; however, the effect of pressure on C16-C34 and C34-C50 fractions concentrations is negligible as there is no significant change observed in the amount of C16-C34 and C34-C50 concentrations by increasing the pressure. Increasing the pressure causes the

concentrations of C10-C16 and total petroleum hydrocarbons to decline to a certain point and slightly increase afterwards.

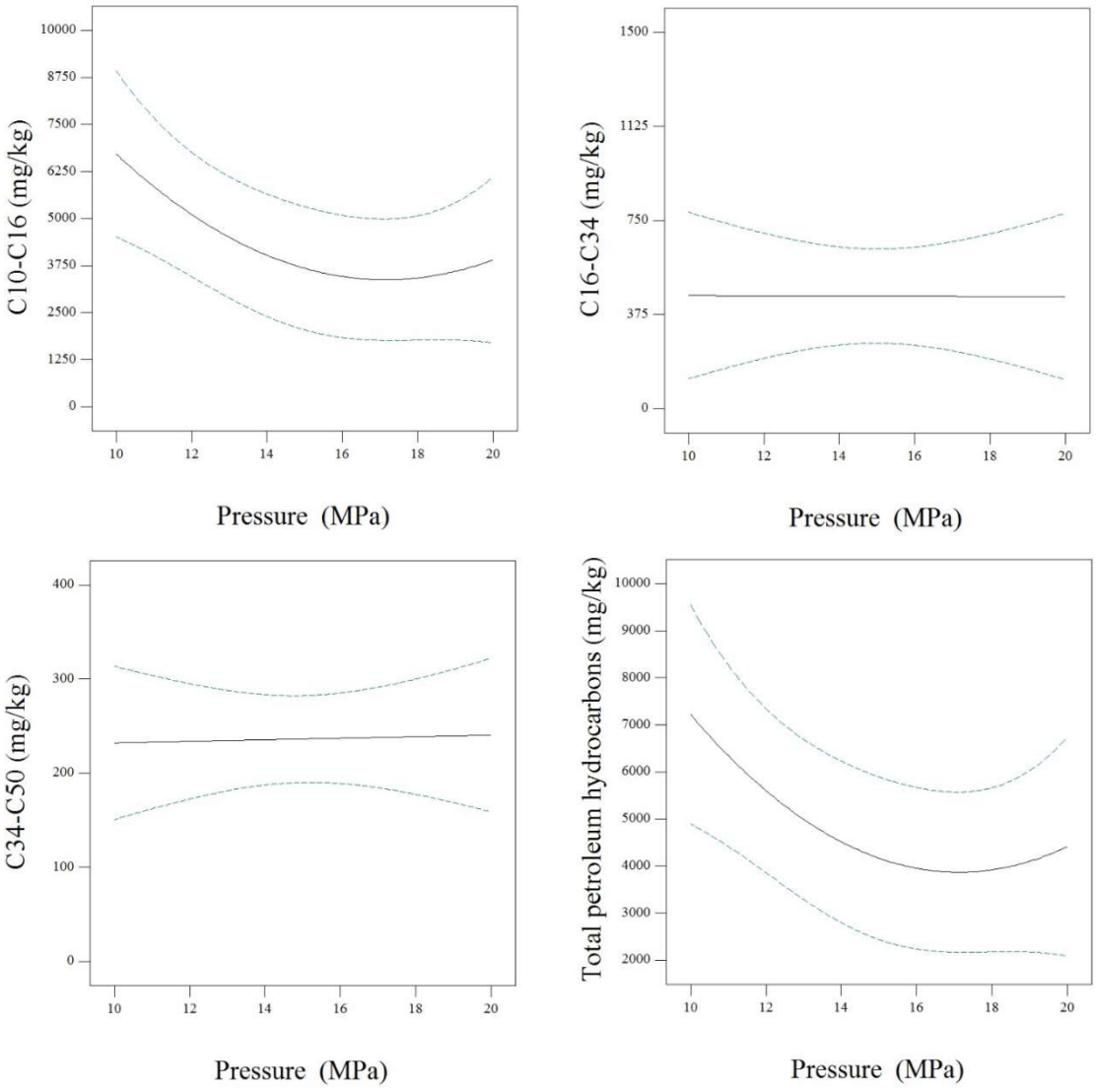


Fig. 5.8 – Effect of pressure on the removal and recovery of petroleum hydrocarbons at a temperature of 50 ºC and a contact time of 75 minutes (Initial concentrations of C10-C16 hydrocarbons: 65,298 mg/kg; C16-C34 hydrocarbons: 34,320 mg/kg; C34-C50 hydrocarbons: 1,800 mg/kg; and total petroleum hydrocarbons: 101,418 mg/kg)

The effect of pressure on the removal and recovery efficiency of the petroleum hydrocarbons for the supercritical CO_2 extraction process is illustrated in Figure 5.9. Similar to the temperature effect, higher system pressures resulted in increased efficiencies to more than 95% and then a slight decrease was observed. Therefore, an optimized pressure needed to be determined to maximize the removal and recovery efficiency. The Design Expert® software suggested a quadratic model for the process efficiency on petroleum hydrocarbon removal and recovery with an R-Squared value of 0.93.

Increasing the pressure may have complex effects on solubilisation, diffusivity, and other characteristics of the supercritical CO_2 (McHardy and Sawan, 1998), that may affect its ability to dissolve and separate the petroleum hydrocarbons from the waste drilling mud. Increasing the pressure of the supercritical carbon dioxide results in increased density and thus improves its solvating power (McHardy and Sawan, 1998). Furthermore, the interfacial tension between CO_2 and the petroleum hydrocarbons was reported to be reduced by increasing the pressure in the CO_2 supercritical state (Wang et al., 2015) to which higher removal and recovery efficiencies can be attributed to. Therefore, it would be easier to remove petroleum hydrocarbons at higher pressures. On the other hand, increasing the pressure of supercritical CO_2 increases its viscosity which has an adverse impact on the solubilisation and removal of organic contaminants. Many authors stated that the increase in the pressure can increase the oil and petroleum hydrocarbons removal and recovery efficiency only up to a certain amount and no increase afterwards could be observed (Odusanya, 2003; Lopez-Gomez, 2004; Saintpere and Morillon-Jeanmaire, 2000).

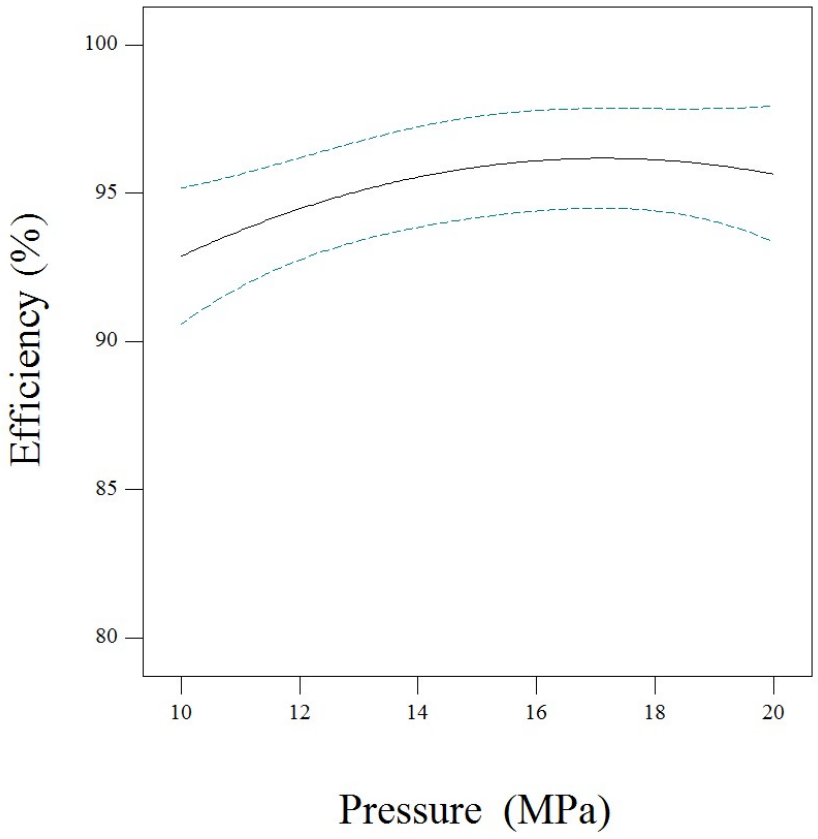


Fig. 5.9 – Effect of pressure on the removal efficiency of total petroleum hydrocarbons for the supercritical CO_2 extraction process (temperature of 50 ºC and contact time of 75 minutes)

5.3.3 Effect of contact time

The effect of contact time on the removal and recovery of petroleum hydrocarbons and the effect of contact time on the removal and recovery efficiency are shown in Figures 5.10 and 5.11 respectively. Hydrocarbon fraction concentrations decreased by increasing the contact time of CO_2 with the waste drilling mud, in different trends, and the removal and

recovery efficiency of petroleum hydrocarbons increased up to 97%. The quadratic model was suggested for the removal and recovery efficiency of petroleum hydrocarbons which reached its maximum value at a contact time of 120 minutes.

The increased contact time can provide sufficient time for the CO_2 molecules to diffuse the particles of the waste drilling mud and separate the oil and drilling fluids retained on the surface of the fine solid particles. The optimized contact time was measured to be 120 minutes.

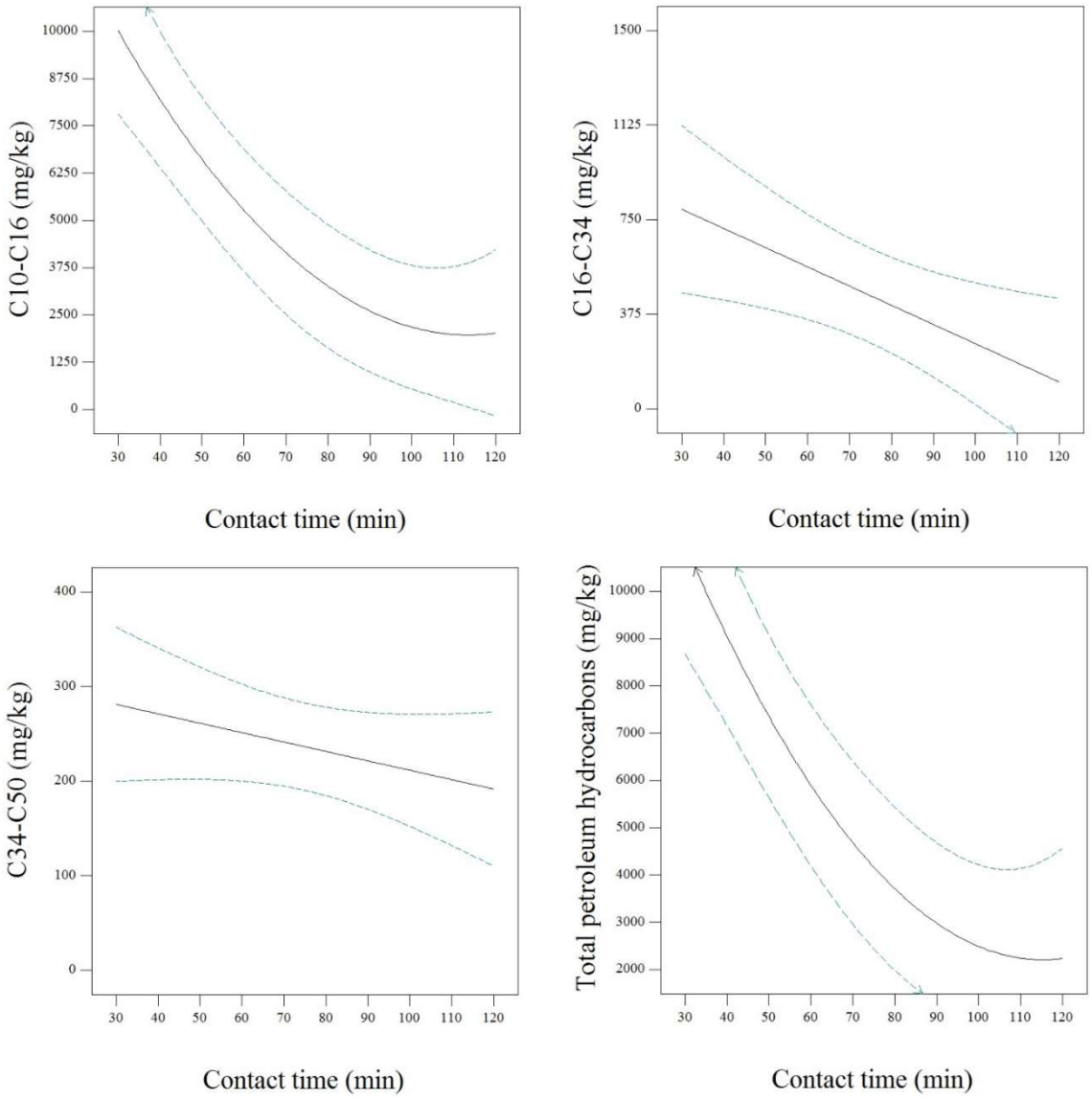


Fig. 5.10 - Effect of contact time on the removal and recovery of petroleum hydrocarbons for the supercritical CO_2 extraction process at a temperature of 50 ºC and a pressure of 15 MPa (Initial concentrations of C10-C16 hydrocarbons: 65,298 mg/kg; C16-C34 hydrocarbons: 34,320 mg/kg; C34-C50 hydrocarbons: 1,800 mg/kg; and total petroleum hydrocarbons: 101,418 mg/kg)

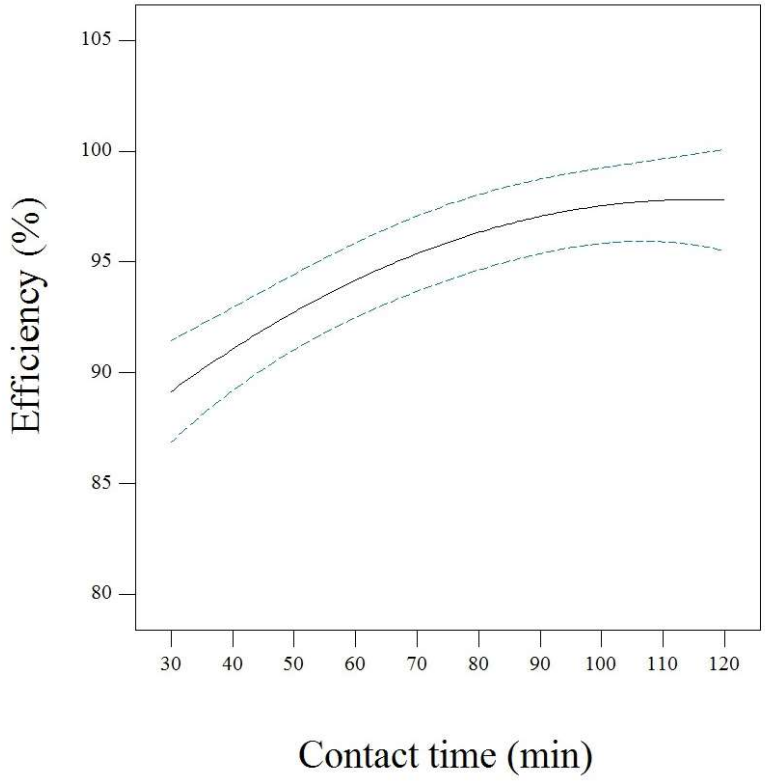


Fig. 5.11 – Effect of contact time on the removal and recovery efficiency of total petroleum hydrocarbons (temperature of 50 ºC and pressure of 15 MPa)

5.3.4 Mechanism of supercritical CO_2 extraction

Supercritical CO_2 extraction showed excellent efficiency of petroleum hydrocarbon removal from waste drilling mud. Due to gas-like viscosities and liquid-like densities of the supercritical fluid i.e. CO_2 above the critical temperature and pressure, CO_2 could rapidly diffuse through the waste drilling mud solid particles like as gas and dissolve materials like a solid. Supercritical CO_2 extraction was studied as a physical treatment

technology where diffusion and dissolution are considered the main petroleum hydro carbon removal and recovery mechanisms. Generally, organic contaminants on solid particles could be present at two states including deposited and sorbed (Berglof et al., 1999). Dissolution can easily remove the deposited contaminants as they are present as a separate phase while sorbed ones may require harsher extraction (Berglof et al., 1999). Solubility of petroleum hydrocarbons in the waste drilling mud could significantly change by alterations in temperature, pressure, and contact time as shown above. Solubility of organic compounds (herein, petroleum hydrocarbons) in the supercritical fluid (herein, CO_2) is also dependant on the complex structure and thermodynamic properties (Anitescu and Tavlarides, 2006) (herein, of the waste drilling mud as well as hydrocarbon-CO_2 interactions). In the present study, the detailed mechanism of supercritical CO_2 extraction for waste drilling mud remediation was not studied in detail. The results of this study can be employed as useful general guides for further mechanism studies; however, in order to understand the SCE mechanism better, detailed studies on the adsorption and desorption characteristics of the organic compounds present in the waste drilling mud would be required and is recommended.

5.3.5 Optimization of the supercritical CO_2 extraction

The Design Expert® software provided the optimum conditions of the supercritical CO_2 extraction process to be at the temperature of 53.5 ºC, the pressure of 18.90 MPa, and the contact time of 120 minutes. Conducting the supercritical CO_2 extraction process at the

optimized conditions will result in a petroleum hydrocarbon removal and recovery efficiency of 97.68%. The desirability of the optimized point was calculated to be 0.988.

5.4 Summary and conclusions

The supercritical CO_2 extraction process was identified as an effective and environmentally-friendly technique to remove and recover the petroleum hydrocarbons from the waste drilling mud. It was observed that the supercritical CO_2 extraction process can achieve up to 97% of petroleum hydrocarbon removal and recovery efficiency in relatively low temperature and pressure above the critical point, and in only 120 minutes.

In this chapter, the supercritical CO_2 extraction process was experimentally tested by designing the experiments based on the Box-Behnken design (response surface methodology) and the process was optimized using the Design Expert® software using three significant parameters namely; temperature, pressure, and contact time. The effects of these parameters were separately identified and a polynomial method was developed to predict the behaviour of the supercritical CO_2 extraction process to remove the petroleum hydrocarbons. Finally, the process was optimized and the optimized operating conditions were also identified.

Chapter 6: Concluding Remarks and Recommendations

6.1 Summary and conclusion

Remediation of slurry waste drilling mud is a significant challenge and various methods have been proposed to meet strict environmental regulations; however, most of them have been considered either too expensive or non-efficient to meet landfilling regulations. Therefore, the main objective of this study was to identify an efficient and environmentally-friendly process to remediate the waste drilling mud to meet strict landfilling regulations. Surfactant-enhanced washing and supercritical CO_2 extraction processes were proposed as two efficient and environmentally-friendly treatment processes. They were experimentally tested for their capability to treat waste drilling mud, and their operating conditions were optimized. There has been little research on surfactant selection for an efficient surfactant-enhanced washing of the waste drilling mud. Therefore, three surfactants were selected based on the literature review and their ability to reduce the interfacial tension. Their suitability for waste drilling mud washing was experimentally tested, and the most suitable surfactant (Triton 100) was selected based on the interfacial tension and sorption analyses. The optimization was completed for the surfactant-enhanced washing based on three significant operating factors: contact time, temperature, and the surfactant concentration. The supercritical CO_2 extraction was also developed, experimentally tested, and optimized using the Box-Behnken design based on three significant parameters, including contact time, temperature, and pressure.

The results suggested that the surfactant-enhanced washing process can partially remove the petroleum hydrocarbons from the waste drilling mud; however, the efficiency is not sufficient to meet the landfilling regulations. It was also concluded that the supercritical CO_2 extraction is an excellent treatment process for the remediation of the waste drilling mud. More than 97% of the petroleum hydrocarbons could be removed and recovered without destroying the solid particles using Triton 100. Therefore, for our waste drilling mud sample, the supercritical CO_2 extraction process can technically be used to remediate the waste drilling mud to meet the landfilling regulations (considering the initial total petroleum hydrocarbon concentration).

In addition to "Chapter 1: Introduction" and "Chapter 6: Concluding Remarks and Recommendations", the dissertation contained 4 Chapters, including:

- Literature Review (Chapter 2)
- Waste Drilling Mud Characterization (Chapter 3)
- Surfactant Selection and Surfactant-enhanced Washing (Chapter 4)
- Supercritical CO_2 Extraction (Chapter 5)

6.1.1 Literature review

The second chapter, entitled "Literature Review", contained detailed information on how the waste drilling mud is produced, its types and composition, and why it is considered a hazardous material. Landfilling regulations around the world and the role of various

treatment technologies to meet the landfilling regulations were also discussed. The advantages and disadvantages of the proposed methods for the treatment of the waste drilling mud (biological, thermal, chemical, and physical methods) were described. It was concluded that physical treatment technologies are suitable processes to be experimentally tested for waste drilling mud remediation due to their high efficiencies on hydrocarbon removal and recovery, relatively low cost, and low environmental impact. Since surfactant-enhanced washing and supercritical fluid extraction processes were considered two efficient and environmentally-friendly processes, this dissertation focused on their development, experimental investigation, and optimization to treat the waste drilling mud.

6.1.2 Characterization of the waste drilling mud

The characterization of the waste drilling mud was presented in Chapter 3. Several characterization analyses were conducted to gain more perspective on the composition, particle size, moisture content, pH, electrical conductivity, and hazardous metal concentrations of the waste drilling mud sample. Tier 1 method was followed to determine the concentration of various hydrocarbon fractions and total petroleum hydrocarbons in the waste drilling mud. The results suggested that the waste drilling mud mainly consists of calcite ($CaCO_3$), barite ($BaSO_4$), and quartz (SiO_2) and thus, possesses a negatively charged surface. It was also concluded that the mud sample has low hazardous metal concentrations and there is no specific treatment required to reduce the metal concentrations; however, the total petroleum hydrocarbon concentration was reported to

be above the landfilling limits. Therefore, development of a treatment method is required to reduce the amounts of petroleum hydrocarbons to meet the landfilling regulations.

6.1.3 Surfactant selection and surfactant-enhanced washing

The methodology and results of surfactant selection and surfactant-enhanced washing were described in Chapter 4. It was explained that cationic surfactants are rarely employed for remediation purposes because they are hazardous to humans and nature, and possess high potential for sorption to solid particles. Anionic surfactants, on the other hand, have the least sorption potential and the non-ionic surfactants are being considered in remediation processes due to their intermediate sorption and their environmental friendliness. For the current study, three surfactants were selected based on the literature review and their capability to reduce oil/water interfacial tension. One anionic (Alfoterra 145-8S 90), one non-ionic (Triton 100), and one non-ionic biosurfactant (Saponin) were selected to be experimentally tested for their capabilities to treat the waste drilling mud.

Interfacial tension analysis was conducted for different concentrations of surfactants and at different temperatures to determine their effects on reducing the oil/water interfacial tension. The effect of adding a surfactant as an additive (sodium dodecyl sulfate, SDS) was also investigated. Sorption analysis was also completed for three selected surfactants. Based on the interfacial tension and sorption analyses, Triton 100 was selected as the most suitable surfactant to be tested in the surfactant-enhanced washing process for the remediation of the waste drilling mud.

Surfactant-enhanced washing tests were conducted and the effects of three significant parameters were investigated, including surfactant concentration, temperature, and contact time. The results of the petroleum hydrocarbon removal and recovery efficiencies suggested that the effect of temperature on the removal and recovery efficiency is not significant, and the maximum petroleum hydrocarbon removal and recovery efficiency can be achieved in the optimum operating conditions of 30 minutes and 0.07 % (wt./wt.%) surfactant concentration (Triton 100). The results suggested that Triton 100 is the most suitable candidate for the waste mud treatment; however, further treatment may be required to reach landfilling regulation limits.

6.1.4 Supercritical CO_2 extraction

The application of the supercritical carbon dioxide extraction process on the remediation of the waste drilling mud was investigated in Chapter 5. Three significant factors were considered, including temperature, pressure, and contact time, and their effects on the petroleum hydrocarbon removal and recovery efficiency were determined. The Box-Behnken design was employed using Design Expert® software to design the experiments and to develop a polynomial model based on the experimental results. The polynomial model based on the experimental results showed that contact time is the most significant parameter affecting the removal and recovery of petroleum hydrocarbons in the supercritical CO_2 extraction process. Analysis of variance was also completed and the results are listed in Appendix V. The results of the petroleum hydrocarbon removal and recovery efficiencies suggested that the supercritical CO_2 extraction process is an effective

and environmentally-friendly method that can remediate waste drilling mud and recover total petroleum hydrocarbons without damaging solid particles. The maximum hydrocarbon removal and recovery efficiency of 97.68% can be obtained at the optimized operating conditions of 120 minutes, 53.5 ºC, and 18.90 MPa. It was concluded that no further treatment is required to reach landfilling regulation limits.

6.2 Limitations

Although the current research results were promising and show supercritical CO_2 extraction as an effective method to remediate the synthetic based waste drilling mud, there are limitations to the research results which need to be addressed if the results are going to be implemented.

- The results of the current research were solely applicable to the specific type of waste i.e. the synthetic based waste drilling mud from the offshore production facilities in Newfoundland and Labrador and any implementation of these results to other types of wastes require further experimental investigation
- Further investigation on the surfactant-enhanced washing process needs to focus on the mechanism of petroleum hydrocarbon removal using Triton-100 with focus on contact times less than 30 minutes
- Surfactant recovery and hydrocarbon separation from the wastewater produced after waste washing with Triton 100 were not studied in the current research;

however, both tasks can be significant challenges to ensure the tested surfactant-enhanced washing process is cost-effective and environmentally-friendly.

- Optimization of the supercritical CO_2 extraction in this study is limited due to the limited range of studied parameters and for a complete optimization, more tests may be required.

- Further experiments on the supercritical CO_2 extraction process need to be conducted to identify the possibility of higher petroleum hydrocarbon removal and recovery efficiencies after the 120 minutes of contact time studied in the current research.

Despite the limitations of the current research results, they can be useful guides for future studies in the field of drilling waste remediation.

6.3 Recommendations

The following are the recommendations of the current research:

- Scale up tests should be conducted in pilot or commercial scale to confirm the results of the laboratory scale tests conducted in this study. More experimental tests are also encouraged to ensure sufficient data are available to proceed further with pilot scale tests.

- Commonly used anionic biosurfactants for soil remediation (such as rhamnolipid) need to also be investigated for their capabilities to reduce the interfacial tension and remediate the waste drilling mud

- Further studies should be completed on the recovery of the surfactant(s) after the surfactant-enhanced washing process to increase the cost-effectiveness and environmental friendliness of the process.

- New biosurfactants, being developed, should be continuously tested on the waste drilling mud to investigate their remediation capabilities and to improve the efficiency and environmental friendliness of the surfactant-enhanced washing process.

- It should also be noted that the remediation process (supercritical CO_2 extraction) recommended by this study is solely applicable for the waste drilling mud sample obtained from offshore, Newfoundland and Labrador, and to implement this technology to new types of waste, more experiments may be required.

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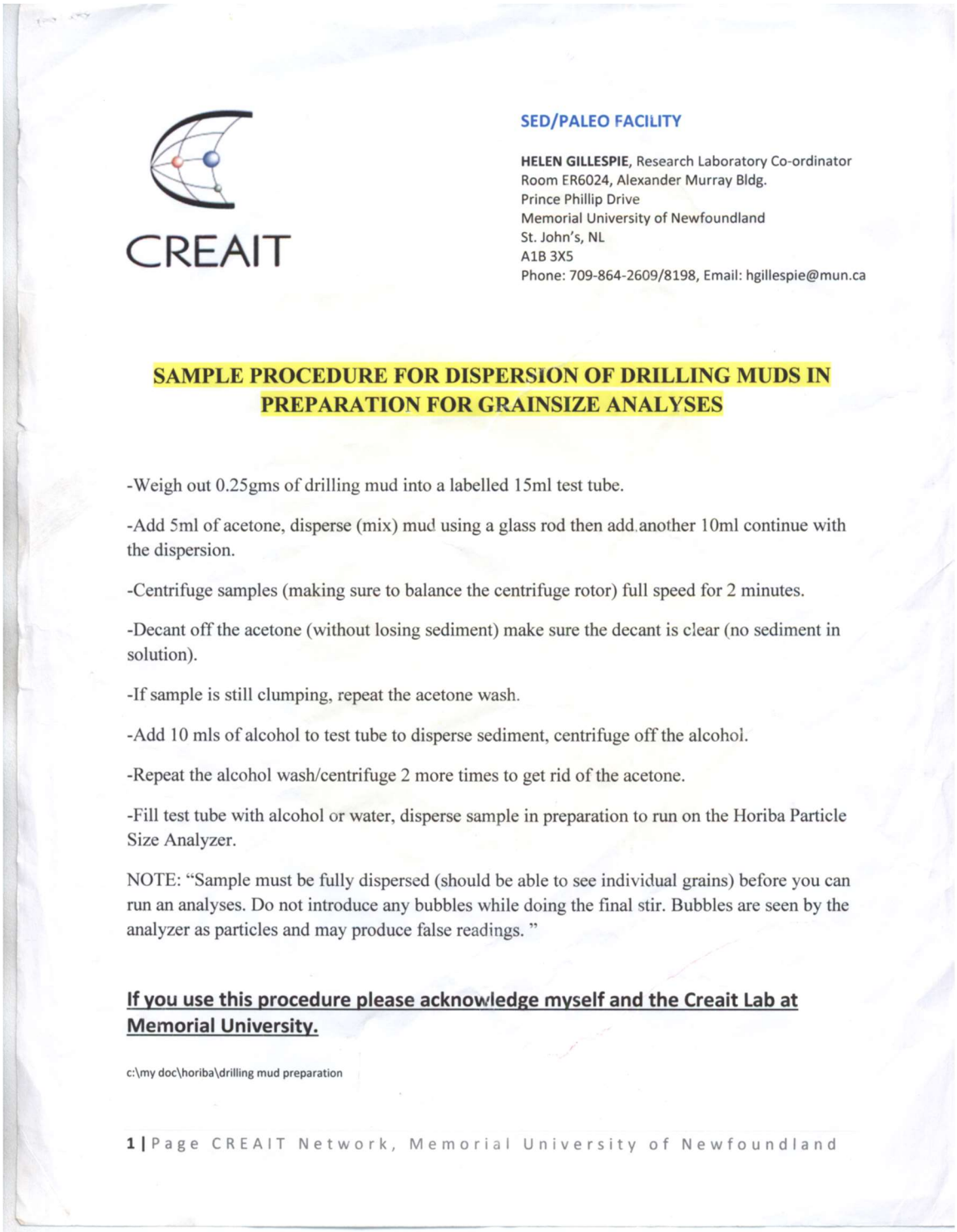
Appendix I. Sample preparation procedure for particle size analysis



CREAIT

SED/PALEO FACILITY

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SAMPLE PROCEDURE FOR DISPERSION OF DRILLING MUDS IN PREPARATION FOR GRAINSIZE ANALYSES

-Weigh out 0.25gms of drilling mud into a labelled 15ml test tube.

-Add 5ml of acetone, disperse (mix) mud using a glass rod then add another 10ml continue with the dispersion.

-Centrifuge samples (making sure to balance the centrifuge rotor) full speed for 2 minutes.

-Decant off the acetone (without losing sediment) make sure the decant is clear (no sediment in solution).

-If sample is still clumping, repeat the acetone wash.

-Add 10 mls of alcohol to test tube to disperse sediment, centrifuge off the alcohol.

-Repeat the alcohol wash/centrifuge 2 more times to get rid of the acetone.

-Fill test tube with alcohol or water, disperse sample in preparation to run on the Horiba Particle Size Analyzer.

NOTE: "Sample must be fully dispersed (should be able to see individual grains) before you can run an analyses. Do not introduce any bubbles while doing the final stir. Bubbles are seen by the analyzer as particles and may produce false readings. "

If you use this procedure please acknowledge myself and the Creait Lab at Memorial University.

c:\my doc\horiba\drilling mud preparation

Appendix II. Results of the interfacial tension analysis

Table II.1. Results of the interfacial tension analysis for our three surfactants at different concentrations

Surfactant / Concentration	Saponin	Alfoterra 145-8S 90	Triton 100
0.1 wt.%	8.35 ± 0.07	7.64 ±0.35	4.58 ±0.01
0.25 wt.%	7.26 ±0.12	6.82 ±0.06	3.23 ±0.29
1.25 wt.%	6.54 ±0.12	5.63 ±0.03	2.75 ±0.10
2.5 wt.%	6.05 ±0.005	4.98 ±0.01	2.00 ±0.05
5 wt.%	5.09 ±0.07	4.57 ±0.09	1.47 ±0.03

Table II.2. Effect of 2 wt.% sodium dodecyl sulfate on IFT at 5 wt.% surfactant concentration

Surfactant	Interfacial tension (mN/m)	
	Without additive	With additive
Triton 100	1.47 ±0.03	2.60 ±0.03
Alforterra 145-8S 90	4.57 ±0.09	5.05 ±0.01
Saponin	5.09 ±0.07	4.29 ±0.04

Table II.3. Results of the interfacial tension analysis for our three surfactants at two different concentrations (0.1 wt.% and 5 wt.%) at different temperatures

Surfactant	**Concentration (wt.%)**	**Temperature (˚C)**	**IFT (mN/m)**
Triton 100	0.1	20	4.58 ± 0.02
		30	4.18 ± 0.01
		40	3.76 ± 0.06
	5	20	1.47 ± 0.03
		30	1.26 ± 0.02
		40	1.23 ± 0.02
Alfoterra 145-8S 90	0.1	20	7.64 ± 0.34
		30	6.71 ± 0.16
		40	5.55 ± 0.12
	5	20	4.57 ± 0.09
		30	3.87 ± 0.04
		40	2.96 ± 0.01
Saponin	0.1	20	8.35 ± 0.06
		30	6.55 ± 0.01
		40	5.94 ± 0.11
	5	20	5.09 ± 0.07
		30	4.56 ± 0.03
		40	4.19 ± 0.02

Appendix III. Results of the surfactant-enhanced washing process

Table III.1. Effect of contact time on the removal of petroleum hydrocarbons for the surfactant-enhanced washing process by Triton 100 (temperature of 30 ºC and concentration of 0.07wt.%)

Contact time (min)	Concentration (mg/kg)				Efficiency %
	C10-C16	C16-C34	C34-C50	Petroleum hydrocarbons	
30	15666.66 ±988	10290.25 ±562	23.03 ±1.02	25979.94 ±656	74.38% ±0.65%
75	19088.02 ±1236	13237.72 ±864	20.58 ±0.98	32346.32 ±870	68.11% ±0.85%
120	21460.89 ±1100	14001.88 ±866	7.56 ±0.5	35470.33 ±535	65.03% ±0.53%

Table III.2. Effect of temperature on the removal and recovery of petroleum hydrocarbons for the surfactant-enhanced washing process by Triton 100 (contact time of 75 minutes and concentration of 0.07wt.%)

Temperature (ºC)	Concentration (mg/kg)				Efficiency (%)
	C10-C16	C16-C34	C34-C50	Petroleum hydrocarbons	
20	22618.74 ±850	9455.69 ±785	48.3 ±0.9	32122.73 ±668	68.33% ±0.66%
30	18418.87 ±802	12310.83 ±621	17.43 ±0.56	30747.13 ±582	69.68% ±0.57%
40	17255.54 ±656	12580.9 ±510	15.25 ±0.46	29851.69 ±479	70.57% ±0.47%

Table III.3. Effect of concentration on the removal and recovery of petroleum hydrocarbons for the surfactant-enhanced washing process by Triton 100 (contact time of 75 minutes and temperature of 30 ºC)

Concentration (wt.%)	**Concentration (mg/kg)**				**Efficiency (%)**
	C10-C16	**C16-C34**	**C34-C50**	**Petroleum hydrocarbons**	
0.05	28273.9 ±1298.5	21523.59 ±980.21	30.25 ±0.25	49827.74 ±939	50.87% ±0.92%
0.07	19478.8 ±588.8	12238.24 ±404.96	12.38 ±0.18	31729.42 ±412	68.71% ±0.41%
0.09	22410.42 ±1147.7	9432.72 ±202.05	124.17 ±11.02	31967.31 ±672	68.48% ±0.62%

Appendix IV. Results of the supercritical CO2 extraction process on the removal and recovery of petroleum hydrocarbons

Run	Temperature (°C)	Pressure (MPa)	Contact time (min)	C10-C16 (mg/kg)	C16-C34 (mg/kg)	C34-C50 (mg/kg)	Petroleum hydrocarbons (mg/kg)	Removal Efficiency (%)
1	60	15	30	9710.8	1080.4	294.6	11085.8	89.1
2	60	15	120	1949.5	145.6	138.8	2233.9	97.8
3	50	10	30	12163.4	112.6	104.3	12380.3	87.8
4	50	15	75	3547.3	316.2	250.2	4113.7	95.9
5	60	10	75	9500.6	77.8	230.1	9808.5	90.3
6	50	15	75	3751.9	240.8	194.1	4186.8	95.9
7	50	15	75	3866.5	221.0	202.5	4290.0	95.8
8	50	15	75	3650.2	224.1	229.5	4103.8	95.9
9	50	10	120	4182.6	334.6	275.9	4793.1	95.3
10	40	10	75	9157.9	1284.2	399.3	10841.4	89.3
11	60	20	75	4984.8	113.2	106.7	5204.7	94.9
12	40	20	75	4545.6	561.1	399.0	5505.7	94.6
13	50	20	30	10235.6	928.3	359.7	11523.6	88.6
14	50	20	120	4001.0	189.9	177.2	4368.1	95.7
15	40	15	30	14661.8	1393.9	290.7	16346.4	83.9
16	40	15	120	4693.2	104.0	99.4	4896.6	95.2
17	50	15	75	3572.7	304.3	266.7	4143.7	95.9

Appendix V. Analysis of variance (ANOVA) of predicted models for supercritical CO_2 extraction

The Design Expert® software suggested linear and two-factor interaction (2FI) models for C16-C34 and C34-C50 concentrations respectively, and a quadratic model for C10-C16 concentration. The model for the removal and recovery efficiency of petroleum hydrocarbons (in terms of coded factors) is listed as Equation V.1. The statistical model obtained by Design Expert® software, using the Box-Behnken design, showed that the removal and recovery efficiency of petroleum hydrocarbons is not solely dependent on the three parameters identified to be significant in the supercritical CO_2 extraction process, but also depend on other interactions. The coefficients represent the significance of various parameters, thus comparing such coefficients can be employed to identify the relative impacts of significant parameters. Equation V.1 can also be employed to predict the response in the provided range for each parameter. The obtained results help to predict the efficiencies when changes occur with some of the factors and to predict the efficiency beyond the designed limits.

Efficiency % = [95.89 + (1.14×A) + (1.38×B) + (4.32×C) + (-0.18×AB) + (-0.64×AC) + (-0.11×BC) + (-1.99×A^2) + (-1.62×B^2) + (-2.41×C^2) **Eq. V.1**

Analysis of variance results for petroleum hydrocarbon removal and recovery efficiency model (R^2 = 0.9281 and Std. Dev = 1.61)

Source	**Sum of Squares**	**DF**	**Mean Square**	**F-value**	**p-value Prob > F**
Model	235.00	9	26.11	10.04	0.0030
Residual	18.20	7	2.60		
Lack of Fit	18.18	3	6.06	1139.03	<0.0001
Pure Error	0.021	4	0.00532		
Correlation Total	253.20	16			

The Model F-value of 10.04 implies the model is significant. There is only a 0.30% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant.